Iron Column near Kotab Minor, Delhi, India. Erected B.C. 900.

Frontispiece.

RUSTLESS COATINGS;

CORROSION AND ELECTROLYSIS OF IRON AND STEEL.

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PREFACE.

Since the publication of the papers "Rustless Coatings for Iron and Steel," in the years 1894–1901, the author has received many requests from engineers and others to present them in a more available form than in the *Transactions of the American Society of Mechanical Engineers* and in the columns of the various American and foreign technical journals. The subjects have been mainly rewritten and new matter added to bring them up to date. The characteristics of oils, pigments, and paints that form the principal protective coatings for ferric and other structures are given at length under their respective chapters. It is believed by the author that the collected data will afford a reliable source of information of what paints are composed and what may be expected of them. The technical journals have given a great deal of space to the subject of proctective coatings for metals, but the data are not always available when comparison with some recent result or experiment is required.

The author acknowledges the assistance afforded him in the collection of the data, by the technical press and nearly two hundred other sources, and he has, as far as possible, given credit for the same.

The subjects are so grouped in the work, and so detailed in the index, that the busy man can find the data that will bear on the case in hand and enable him to avoid some, if not all, of the unfavorable results that have attended previous applications of some misleading trade-mark mixture. Most of the analyses and tests of the commercial pigments and paints have been repeated many times without any material discrepancy from the data herein given. The results from the use of many of these paints are apparent in the excessive and continual corrosion of important ferric structures everywhere. He that runs may not always read, but he can at least see; hence should be able to profit by the experience of those who have preceded him.

M. P. Wood.

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RUSTLESS COATINGS.

CHAPTER I.

PAINTS: OF WHAT COMPOSED, HOW DESTROYED, CLASSIFICATION AS TRUE PIGMENTS AND INERT SUBSTANCES, ADULTERANTS, ETC.*

WHAT is paint? This question can be answered in a broad way by saying: It is any liquid or semi-liquid substance applied to any metallic, wooden, or other surface, to protect it from corrosion or decay, or to give color or gloss, or all of these qualities, to it.

A better definition would be, that paint is a compound of a pigment and a liquid, usually applied to any surface with a brush, for the purpose of protection, or to secure artistic effects; which liquid, after undergoing certain changes, in part mechanical, or chemical, or both, has the power of holding the pigment to the coated surface. It is evident that the latter definition would also include those compounds which are applied to many surfaces either hot or cold as a bath, rather than by a brush, solely as a matter of convenience or rapidity; and particularly so when metallic members of large size, or with intricate and hidden parts, are to be protected.

The essentials of a good paint, for whatever use intended, are:

First.—That it shall adhere firmly to the surface over which it is spread, and not chip or peel off. It must be non-corrosive to the material it is used to protect, as well as to itself under long periods of atmospheric exposure and chemical changes. It must form a surface hard enough to resist frictional influences, yet elastic enough to conform to all changes of temperature, or with a coefficient of

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* Excerpts from a paper by the author presented at the Detroit meeting (June, 1895) of the American Society of Mechanical Engineers, and forming part of Volume XVI, paper number 637, of the *Transactions*.

elasticity approximately as near the material it covers as possible. It must be impervious to and unaffected by moisture, atmospheric or other influences to which the structure may be exposed.

Second.—That it shall work properly during its application—a property which depends largely upon the relative amounts of pigment and liquid. The natures of both pigment and liquid also have influences that govern results.

Third.—That it shall dry with sufficient rapidity. This function depends mostly upon the vehicle or liquid used with the pigment, though the pigment has in many cases an influence, as will be seen further on.

Fourth.—That it shall have proper durability, which is a function both of the pigment and liquid. And as the question of cost is in many cases the governing factor in the selection of a paint, the question of durability may be regarded as the most important one of the list. It should be understood, however, that a paint can be durable *per se*, and not be protective in the strict sense of the word, as can be illustrated in the case of a good paint applied to the surface of a sheet of iron coated with rust. The liquid element in the paint will not absorb or neutralize the corrosion which it covers, but will dry regardless of it, and permit the destruction of the metal to progress beneath its coat.

Fifth.—*Covering power*, by which is meant the power of a pigment so to cover the surface to which it may be applied that its protection from decay is not only assured, but that the minimum amount of paint shall effect this purpose.

The covering power is also used to express the power of a pigment to protect the oil from decay, in which case a large amount of pigment and a small amount of oil are used. This description of paint dries more or less "flat," the pigment being exposed to the weather and held in place by the thin film of oil. It is thought by many master painters that this is the most durable and best paint for general use. On the contrary, paints that dry with a gloss have a large amount of oil and a small amount of pigment, in which case the oil covers and protects the pigment.

It may be used to express *the amount* of color upon the surface; as, generally, if a surface has plenty of color upon it the covering power is said to be good. To illustrate this definition: If an iron-oxide paint is proportioned so that the ratio between the pigment and the oil is by weight 50 per cent of pigment and 50 per cent of oil when the paint is ready for spreading, and the pigment consists of 30 to 40 per cent of iron oxide, the covering power will be said to be good; but if the same proportions of 50 per cent ratio between the pigment and the oil be had, in which the iron oxide is only 5 per cent of the pigment, the covering power would be called poor; and so it would be in the case where 10 per cent of pigment and 90 per cent of oil were used. If in the two latter cases the oil contained large or liberal amounts of volatile diluents, the appearance of the surface would indicate a deficiency in the covering power of the paint.

The *covering power* is also commonly expressed in the amount of surface which a given *weight* of paint will cover. A good iron-oxide paint will cover nearly twice as much surface as white or red lead. The *specific gravity* of the paint also is to be considered in the definition of this power. The lightest paints have the most covering power. White lead is about 6.4 times as heavy as water; iron oxide 5 times; yellow ochre 3½ to 4 times, etc., etc. With this variation it is manifestly almost an impossibility to get the same number of particles of the same size out of the same weight of different materials.

Fig. 1 represents the covering power of a number of paints and inert pigments.

The refracting power of light has much to do with an understanding of this covering power of paint. The greater the refracting power of the pigment is over that of the oil, the better will be the covering power. The index of refraction of air is 1 degree; water, 1.34; linseed-oil, 1.48; glass, 1.50 to 1.55; silica, 1.55; feldspar, 1.54; whiting, 1.65; chrome-yellow, 3.00; vermilion, 3.20, etc. There is no exception to the rule that the finer the state of division to which *any* pigment is reduced, the better will be its covering power. Sulphate of lime, barytes, feldspar, silica, talc, whiting, etc., are all of low refractive power, and of themselves, independent of this refractive quality, do not constitute good pigments, though when mixed with the metallic pigments and ground together in the oil the result is a pigment of good covering power, almost as good as the best one of the combination. For instance, 80 per cent of sulphate of lime and 20 per cent of zinc white, form a pigment almost as good as all zinc white, and 10 per cent of white lead and 90 per cent of talc carefully ground, give a very satisfactory result so far as relates to the covering power; but all of the above and other kindred compositions, while improving the covering power, are to be classed as *adulterants,* the use of which is objectionable so far as durability and protective power are concerned.

The covering power is due to two qualities. For instance lime whitewash has very little covering power until it becomes dry. Barytes covers well as a water paint, because the water leaves it as a dry powder on the coated surface. But barytes covers poorly in oil, because the oil remains with it, and the light reaches it through the transparent film of oil.

Fig. 1.—Covering power of paints.

Prof. Von Bezold's experiments,* from which I quote, illustrate how lime, barytes, white lead, and other crystalline pigments, when mixed in oil, become more or less translucent, and therefore do not *color* the surface that they *cover*.

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* Von Bezold. "Theory of Color." L. Prang Co. Condict's "Painting and Painting Materials."—*The Railroad Gazette.*

"If a small glass test-tube be partly filled with powdered glass, the powder will appear white, and it will be impossible to see through it, but as soon as water is poured into the tube, the powder, to a certain degree, becomes translucent. By substituting turpentine for the water, the degree of translucency is materially increased. If a small quantity of sulphuret of carbon is added to the turpentine, a liquid is obtained that reflects (bends) the light about as powerfully as glass. If some of this liquid be poured upon the powder in the test-tube, the powder will disappear, and light passes through the tube as freely as though no powder were present.

If a solid glass rod be immersed in such a liquor (or a mixture of olive-oil and oil of cassia), it will appear as if the rod only reached to the surface of the liquid. Within the liquid the rod cannot be seen (Fig. 2).

It is shown by these experiments that the presence of one transparent body within another is only detected by the eye when the two differ in their power of refracting light.

Many white substances are white because they are in fine particles. A white lily is white because it consists of little cells which reflect all kinds of light, again and again, until it reaches the eye from some part of its surface. Water becomes white when it is broken into fine drops, as in a waterfall or on the crest of waves. White lead and zinc owe their whiteness to their dense, fine, powder-like condition, and transparent glass becomes white when finely pulverized."

Fig. 2.

As stated before, the finer the pigment is subdivided, whether as a paste which is afterward thinned with oil or volatiles to a consistency to spread with a brush, or is ground in the oil direct (a process that all pigments will not endure without injury to their color—the scarlet lead chromate, for instance) to the proper consistency to spread, the better will be its covering power.

An ounce of lampblack, because of the minuteness of its particles, will cover more surface in an effectively protective manner than any known pigment, and one part lampblack and nine parts sulphate of lime by weight, give most excellent results in covering power. Prussian blue, the scarlets, lakes, and others of what can be called "the fugitive colors," on account of their tendency to fade out, possess the *light-dispersing power* which deceives the eye as to their covering power, when in reality for actual covering as protective substances they are absolutely worthless. These colors should be denominated stains rather than paints; for generally the only measure of protection from decay or corrosion which accompanies their use is solely from the oil or liquid with which the color is mixed.

The designing of a paint, for whatever purpose, necessarily includes the qualities already mentioned, viz.: adhesion and elasticity, working qualities, drying qualities, durability, covering power. The other quality, the cost, cannot be ignored, and will be duly considered later, as well as what pigments to use for the intended purpose. All pigments do not contain all of the above qualities. The question naturally arises: Is it necessary for a pigment to be pure and unmixed with inert substances, or can a certain amount of these be mixed with the pigment without detriment to it?

Experiments of long duration lead to the conclusion that the oxides of iron, lead, manganese, and other strong pigments, can be mixed with large amounts of these inert substances without detriment, and generally to the manifest improvement of the paint as a protective agent on many structures, notably *wooden or composite ones.* A single illustration will suffice to make this apparent. Oxide of iron is one of the strongest of pigments in covering power. If one ounce of this pigment be spread in two coats over a given surface, say two square feet, so that the surface be completely hidden, and the job be declared a satisfactory one so far as covering power is concerned, and in the second case an ounce of the same oxide of iron be mixed with three ounces of barytes, kaolin, gypsum, etc., and this paint be spread over two square feet of surface as before, it is obvious that the amount of color per unit of surface will be the same in both cases; but in one case there is four times as much pigment as in the other, and in the second case three-fourths of the paint would be inert material. For railway cars and wooden structures the durability of these paints would be in favor of the second case, as well as the cost of the paint. The pigment in this case is the life of the paint, and protects the oil from the decay incident to oxidation from atmospheric exposure.

Oxide of iron is practically unchanged after centuries of exposure. It induces and promotes oxidation in all organic substances with which it is brought into contact, and in nearly all metallic bodies. In an oxide-of-iron paint it is the oil which decomposes, it being the organic matter. The decomposition is due to the exposure to the elements aided by the oxidizing power of the oxide of iron pigment mixed with the oil. This statement holds true only where there has been no chemical change or combination between the pigment and the liquid.

Whiting, sulphate of lime, barytes, kaolin, silica, feldspar, and talc are the principal inert substances used in pigments. Whiting, gypsum, and barytes are the best of the list; the others, grinding greasy, are hard to grind, or of a nature readily decomposed by water, are objectionable. Barytes, from its great weight, is objectionable as a paste or prepared paint. Its use as an adulterant is given in Chapters VI and XVIII. The sulphate of lime (gypsum) is no doubt the best of the inert substances to mix with any pigment, all things considered. It should be thoroughly hydrated. As high as 45 per cent by weight of this substance can be mixed with 50 per cent of sesquioxide of iron for a pigment. Many of the oxide-of-iron paints are made by ignition of copperas, and a notable amount of sulphuric acid is usually left in the oxide which the heat has failed to drive off. From 2 to 5 per cent of carbonate of lime is added to neutralize the free acid, changing it to sulphate of lime. In these proportions, the pigment really consists of 50 per cent of oxide of iron and 50 per cent of inert material, all by weight. Any oxide-of-iron paint which contains hydrated oxide or free SO_2 will deteriorate rapidly by oxidizing the liquids, while any free SO_2 will retard the drying of the paint.

A good paint prepared for spreading in ordinary temperatures upon wooden or composite structures has the ratio by volume of about one-third pigment and two-thirds oil or liquid. The practice upon one of the leading railways of the United States, where the materials purchased for paints amount to over $300,000 yearly, is to allow 75 per cent of pigment and 25 per cent of oil by weight, for the paints applied to cars and wooden structures.

Experiments determine that the most durable paints are those which contain a large amount of pigment per unit of surface; and that pigment is the best which is strong enough of itself, or with a proper proportion of inert material, to allow liquid enough to be added to it to flow and work well with the brush when applied.

Destruction of Paint.

The destruction of paint may be from eight causes: *First,* mechanical injury; *second,* the action of deleterious gases; *third,* chemical action between the pigment and the vehicle or liquid; *fourth,* chemical action between the body covered and the paint, either the pigment or the liquid; *fifth,* the action of light; *sixth,* peeling; *seventh,* destruction by cleaning; *eighth,* water.

Many master painters and manufacturers claim that the destruction caused by cleaning and the action of water are the worst of the above causes. This is true so far as paint applied to *wooden structures* is concerned, but has no relation to the causes which effect the destruction of paint applied to iron or steel structures. As most of the above destructive agents are common to all structures (wooden, metallic, or composite) which depend in a greater or less degree for their preservation from decay or corrosion, upon paint (under which name all paints, oils, varnishes, japans, and surfacers are classed), it may not be amiss to discuss briefly each of these causes in detail before citing the destructive agencies which relate solely to the corrosion of metallic structures, the prevention of which will require the consideration of other preservative methods than paints, or which may be used in connection with paint to secure the best protective results.

First.—Mechanical injury to *wooden structures* is not a serious cause of deterioration of paint. Near the seashore the wind and sand have the effect of a sand-blast, which cuts away the paint rapidly, and in this case the more elastic the paint, the less will be the mechanical injury. This sand-blast action is quite as effective on ferric structures, and as generally they are of a more important character than the wooden cottages and minor buildings on the seacoast, its action must be guarded against. If the paint coating is of a soft, spongy nature it will resist the sand-blast, but will absorb moisture from the air, and hasten either the oxidation of the paint or the metallic surface which it covers.

A further injury to metallic structures can be classed under the head of mechanical, viz.: that arising from the expansion and contraction of the various parts from the atmospheric changes which are constantly going on, changes ranging from 40 degrees F. to 150 degrees F. not being unusual. It is an impossibility to proportion a paint compound so that its coefficient of elasticity will be the same at all temperatures as that of the metal it covers. It may be possible to do this at some temperature at or between 60 degrees and 90 degrees F., or even between +40 degrees F. and 90 degrees F.; but that any paint in the class of commercial colors will do this at all temperatures is the tale of the salesman. It may be argued that, these changes coming from the external surface of the paint and being transmitted through its coating, it will be the first to adjust itself to the new or varying relation between the metal and the paint, and so will work to the advantage of the paint in making the change, this being in ordinary cases a gradual one. If the paint is of an elastic, close-clinging material, and not a hard, vitreous one, the claim will hold good.

The compounds which most closely partake of this nature, will be spoken of hereafter. An addition to this problem will be had when the strains due to the action of wind, the passage of railway trains, and those due to changes of a sudden and vibratory character, together with the action of snow, hail, and water driven at high velocities, are added to the temperature changes. These strains necessarily come to the metal first, and whatever changes occur in the bars by the strain, the paint must accompany them. As these strains are generally of a vibratory or percussive character, it can easily be seen why they should be classed in the list of mechanical injuries. In fact, they are a succession of blows which the structure must absorb, withstand, and extinguish within itself or its connections; the structure then returning to its normal condition, the paint or other protective covering must accompany it, instead of loitering by the way and being grounded or "left" in the chain of operations.

Second.—The action of deleterious gases is very familiar to those who have studied paints and protective compounds. Sulphuretted hydrogen is one of the most common and active of these gases, and is formed in excessive amounts wherever coal is distilled for illuminating gas. Sulphurous acid fumes also, being disengaged in the combustion of coal in the many arts, transportation, and manufacturing processes of the day; gases engendered in workshops, being of a compound character carrying ammonia, carbonic acid, nitric acid, and other fumes, are active agents of corrosion to metallic bodies, also to the paint compounds that cover them. (See Analysis of Smoke, Chapter XXXVI.)

Third.—Chemical action between the pigment and the vehicle. This is an exceedingly important field of inquiry, and largely an unknown one. Many of the siccative and other oils which are in common use for paints are capable of saponification. It is well known that soda and potash are not the only substances which combine with fats to produce soap, and that almost any of the bases can be combined with the fatty acids of nearly all oils to make soap, hence we have iron soap, lead soap, zinc soap, manganese soap, etc. Many pigments are simply oxides or hydrates, in the same way that soda and potash are, and it is strongly suspected that they combine with the oil to form soaps, in which case it will be evident that, after the paint has been left on the surface for a number of years, instead of a pigment held to the surface by the liquid and which has undergone certain changes called "drying," it is in reality a new chemical body consisting of the constituents of the liquid combined with the pigment, or in other words, it may be a soap.

Fourth.—Chemical action between the body covered and the paint, either the pigment or the vehicle. The chemical changes which may or do take place between the pigment and the liquid as set forth in Article III, can be supplemented here to embrace those paints which contain pigments, one or more of which give up oxygen or break down in the presence of organic matter—the oil or liquid of the paint. Hydrated oxide of iron (iron-rust) oxidizes organic matter (the oil) and gradually destroys it. Oxide-of-iron paints of all kinds gradually grow darker with age from the oxidation of the oil, this oxidation progressing until either the paint cracks and falls off as a scale on any mechanical disturbance, or is washed away in the process of cleaning or by the action of storms. Chromate of lead, bichromate of potash, the chlorates, magnanese dioxide, red lead, and a number of other pigments also possess this oxidizing power to a great degree.

Fifth.—The action of light. The action of light as a bleaching element is well known in almost all fields of human industry; but the chemical changes which occur between the pigment and the liquid are not well understood, this action being furthermore complicated by the different temperatures to which the coated surface may be exposed, and aided by the effects of sea air or fumes from various manufactories. We know that certain pigments fade upon exposure, whether applied to metallic or other structures. The pigments which contain organic coloring-matter from coal-tars, dyewoods, etc., fade more rapidly than those which have a metallic base; but it has never been established that the bleaching of the paint in all cases *detracts* from its durability.

Sixth.—Peeling. Paints vary greatly in their power to adhere to either metallic, wooden, or other surfaces; notably zinc white, which peels under almost any condition or from any surface to which it may be applied. There is no other pigment which possesses this property in so marked a degree, and it is difficult to assign any reason why it should peel so badly. A possible cause is that the zinc white combines with the oil used in the paint and forms one of the compounds known as metallic soap, this particular one being zinc soap, a hard, brittle, non-adhesive substance, easily removed by mechanical injury, water, and in the process of cleaning, etc. Galvanized iron possesses the property of causing almost any paint applied to its surface to peel; in fact, it is one of the worst substances to cover with a pigment in a satisfactory manner. Experiments made by a leading railway company in the United States, in which a number of the best pigments in use by that company for all descriptions of railway work were tried upon galvanized-iron car-roofs and other galvanized work, cornices, etc., showed at the end of three years that but one of the list was in any manner satisfactory, and this one was a patented compound with bisulphide of carbon as the vehicle. Ordinary trade colors are of the most unreliable nature when applied to galvanized iron exposed to the trying conditions of railway service. Various reasons have been given for this peculiar action of paint upon galvanized iron. One of the most plausible is that the use of sal-ammoniac in the process of galvanizing causes the formation of a thin film of the basic chloride of zinc on the surface of the metal being galvanized, which material, being of a hygroscopic nature, acts as a repellant to prevent the close adherence of the paint to the metal, and the pigment dries as a skin over it. Sheet zinc does not hold some kinds of paint. Sheet lead also is difficult to cover, and paints which take tin and lead will not always adhere to zinc. As a general rule, the strong oxide paints take these metals better than talc, ochre, and the earthy pigments. No positive general statement can be given, and the problem of the adaptability of paint to a metal to prevent peeling still needs study for each application. Paints applied in cold weather, and which are exposed to a frost while drying, will always peel, unless the paint is warmed to about 120 degrees F.

Another fruitful cause of the peeling of paint is when the several coats are successively applied before the foundation or preceding coat has thoroughly dried, the result being that the liquid in the outer or last applied coats, softens those previously applied. The resulting mass, containing a notable amount of the more volatile elements of the liquid, beginning to dry from the outside surface, forms a thin but hard or vitreous surface which retards the further evaporation of the volatiles and prevents the access of oxygen from the air, which is necessary in the process of drying. If the surface thus covered has been painted while at a low temperature or during a damp or foggy atmospheric condition, and soon after there is a marked rise in the temperature or a fall in the hygroscopic condition of the atmosphere, then the paint is liable to peel at once, or soon after the change. This effect is hastened where the coating is a heavy one, or one hard to spread by reason of the earthy or inert substances in the pigment, or if benzine has been used as a drier.

As a general rule, *the more substances* that enter into a paint, either as pure pigments, inert substances, or in the composition of the liquid, the more liable it is to peel. A small amount of fish or animal or non-drying vegetable oils, though oxidized by the addition of metallic salts and used in connection with linseed or other siccative oils, also hastens and provides for the certainty of the peeling.

The peeling of paint from wooden surfaces is very common, particularly if applied on unseasoned lumber that contains moisture and air in the cellular formation of the wood as shown by the cut. The air and moisture in the cells expand upon a slight rise in temperature, and in their efforts to escape through the dried paint-skin, push it up in the form of blisters that contain the condensed moisture, and results in the peeling of the paint in blisters or in strips.

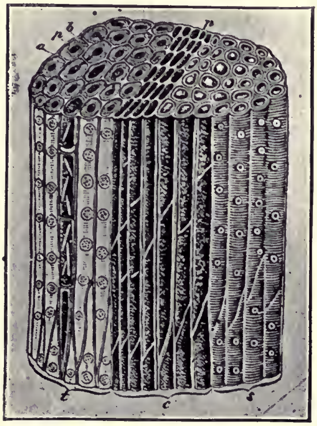

FIG. 3.—Cellular formation of wood causing the peeling of paint.

A pigment composed of a number of substances, the different materials of which by themselves would form the basis of a good paint, when combined together with the liquid, necessarily undergo a different chemical action than the several members of the pigment would have done had they been used alone. This chemical action is furthermore complicated by the combinations going on in the liquid, which, formed of a number of different elements that act and react upon one another, and mixed with the heterogeneous pigment, develop a series of chemical actions in the mass, the weaker element of which, either the mineral or the organic, is the first to break down or change, the decay of which hastens the decomposition of the others and releases the bond between the paint and the surface over which it is spread, and the peeling process is effected.

That these chemical changes exist in the above stated case cannot be denied, but have not been well accounted for. The fact remains, however, that certain paints peel, and though analysis of the peeled portion may reveal nothing to indicate the reason for the peeling, it is seldom possible to get a sample of the original paint applied, to compare its constituents with the peeled sample, and the cause is relegated to the hidden drawer of the paint-shop, near which some scapegoat can be found to bear the burden of failure. (For other notes on the peeling of paint, see Index.)

Seventh.—Destruction by cleaning. This cause of the deterioration and destruction of paint applies more particularly to wooden structures, railway cars, and kindred objects, than to those of a metallic character. It may be sufficient to say we do not wash down an iron bridge, roof-truss, or steamship, with a view to its presenting a clean face for inspection and painting. Almost all the binding materials of dried paints and varnishes are more or less acted upon by caustic and carbonated alkalies, and but little of the soap in the market is free from these substances. The detergents sold for cleaning are all mixtures of sal-soda and caustic substances with lime, pumice, and other inert materials, and the more effective they are for removing dirt, the better they are for the destruction of the paint. If, in the economy of domestic household matters, two removals are equal to one fire, then it may be cited with equal force that two good scrubbings with any washing compound, and most of the soaps of commerce, applied with a stiff brush, will be equal to the next painter's bill to restore matters to their pristine state. Aside from the element of cost, it is no doubt the better practice, so far as the ultimate preservation of any metallic structure is concerned, that it should be washed clean with some of the detergent compounds of the day, in a very weak solution to remove the dirt, then sponged with a liberal amount of clean water, then be allowed to dry thoroughly before the new paint is applied; but I must confess as an engineer, that the above method of painting is rare, and that the rule is for the paint to be put on regardless of cleaning the old coat, and, like Charity, trust it to cover the sins beneath.

Eighth.—Water. The destructive action of water upon paint applied to structures of any material, either upon their internal or external surfaces, is very strong, and will rank next in destructive qualities to the detergent soap and scrubbing-brush. Inside painting lasts longer than outside, principally because it is less exposed to the action of water. Direct experiments show that dried linseed and other siccative oils, without pigment, are not resistant or water-repellent. When the oil is well dried, the application of water always causes the oil to assume a shrivelled appearance, showing that it has absorbed moisture and expanded, and disintegration has commenced. If the exposure be long continued, the whole coating of dried oil will slump away from the surface over which it is spread. Rain-water, from the sensible amount of ammonia that it carries, increases this destructive action on the dried oil, and the slow wasting away of good paints containing pigments best known to resist aging influences, and which have been hardened by time, can be attributed to this action.

The ordinary test by master painters, of the ability of an oil or paint to resist moisture is to coat a surface, usually of glass, and when well dried, to immerse it in water for a few hours and note the changes in color and integrity of the paint.

Dr. Dudley's experiments for the Pennsylvania Railroad, on the action of water upon paints, are interesting from the care which was exercised in making them and recording the results. Several samples of a paint designed for use upon cars and wooden structures were made with raw linseed-oil and a very small amount of japan; the same liquid being used for all the samples with varying amounts of pigment, all the proportions being by weight. Two coats of these paints were spread upon glass, and allowed to harden for two to three weeks. These samples were then placed side by side, and a small portion of the surface of each covered with a globule of water. This globule was covered to prevent evaporation, and then allowed to stand for twelve to fourteen hours.

No. 1 was the linseed-oil and japan alone.
" 2 " same liquid 90 parts, pigment 10 parts.
" 3 " " 80 " 20 "
" 4 " " 70 " 30 "
" 5 " " 60 " 40 "
" 6 " " 50 " 50 "
" 7 " " 40 " 60 "

By weight.

When the proportions are higher than liquid 40 parts and 60 of pigment, the paint will not spread well with a brush if the liquid is linseed-oil and the pigment has the specific gravity of ordinary oxide-of-iron paints.

At the end of the period named, the behavior of the samples was as follows: No. 1 coating was found to have cleaved off the glass and had become shrivelled wherever the water had touched it. Apparently the dried linseed-oil had soaked up water, much as a sponge acts as an absorbent. On allowing the water to evaporate, the coating dried down again, but not uniformly, and was apparently weakened in texture.

No. 2 showed the same characteristics.

No. 3 showed the same, but in a less degree.

No. 4 did not cleave off the glass, but showed where the water had stood.

No. 5 showed a spot in the same way, but in a less degree than No. 4.

Nos. 6 and 7 showed but very little action.

It can be noted that here linseed-oil dried for some two months absorbed less water than freshly dried oil, while very old dried oil lost this absorbent quality and became almost water-repellent.

To successfully design a paint which will resist all of the previously named destructive agencies, is a difficult matter. The field is an enormous one to cover and but little positive knowledge has yet been obtained, though the investigators and experiments have been legion, and the literature on the subject embraces volumes. Time is an essential factor in the test of the qualities of a paint, and if the experimenter is required to wait five or ten years to determine the merits of any paint, or what effect a slight modification of the proportions has upon any one or more of the eight destructive agencies heretofore stated, a life could be spent and possibly no conclusion reached.

Experiments are numerous in the field of designing a water-proof coating to be applied over the pigment which has been found to possess the most preservative qualities, independent of the water-repellent features, but the goal is not yet reached. How effectually a thin coating of the proper material can protect the surface of a paint which it covers, can be seen in the lettering of old sign-boards, which is perhaps an example of the most durable paint of which we have any record.

This protective effect is explained by the well-known fact that lampblack is one of the best *water-repellents* known, that it is practically indestructible by oxidation or acids, and being *per se* of an oily or greasy nature, when mixed with a pure oil (linseed in these cases), and being in a measure elastic, it has effectually preserved the surfaces and not allowed the water to reach the underlying coats of white lead.

Having set forth the general character of what a paint should be for the purpose of protecting structures from decay or corrosion, and having indicated the most effective causes which provoke or promote the destruction of the object and its protector, it may not be amiss to speak more definitely upon those materials which enter into paint compounds which yield the best results in general practice. These results are based upon the experience thus far at hand as recorded or accepted data, and not the hypothesis of some person or persons whose single or joint lives may be too short a period, as compared with the life of the structure they are striving to protect from decay, to realize the meritorious features of their experiment.

CHAPTER II.

PAINTS: STATISTICS AND GENERAL CHARACTER.

THERE are in the United States at the present date (1903) about 420 firms engaged as manufacturers and compounders of pigments, pastes, and paints of all grades, representing a yearly output equivalent to about 90,000,000 gallons of mixed paints, that cost not far from $65,000,000.

This represents about 570,000 short tons, and would cover with one coat 900,000 acres or 1400 square miles of surface, requiring 50,000 painters to spread it.

The following details are the average amounts of the principal pigments used in the United States for the years 1898 to 1902:

Iron oxide,	23,500 short tons.	Value $10.75 to $11.00 per ton.
" "	7,000 " "	" 9.00 for mortar colors.
White lead ground in oil,	85,100 short tons.	Value 5.25 to 5.50 cents per pound.
" " dry.........	25,100 " "	" 4.70 to 4.90 " " "
" " imported....	300 to 700 tons.	
Red lead	11,100 short tons.	" 5.30 to 5.50 " " "
" " imported......	400 to 800 tons.	
Litharge	11,000 short tons.	" 5.30 to 5.80 " " "
" imported......	40 to 350 tons.	
Orange mineral	10,200 tons.	" 7.25 to 7.50 " " "
" " imported	500 to 700 tons.	
Zinc oxide	40,200 tons.	" 4.00 to 4.25 " " "
" " imported in oil	16,000 " Dry, 250 tons.	
Flake graphite.........	1450 tons	Value 5.50 to 6.25 " " "
Amorphous graphite.....	2500 "	
Acheson's "	30 "	

Imported graphites of all grades average from 10 to 12 times the amounts produced in America.

Ochres of all grades were produced in 13 different States, Pennsylvania furnishing over one-half of the entire output of 14,200 to 14,500 short tons. Value $6.50 to $7.00 per ton.

Imported ochres, 7,700 to 8,000 tons. Value $7.70 to $7.90 per ton.

Spanish brown, principally from Maryland, 600 to 650 tons. Value $17.70 to $18.00 per ton.

Approximately, the United States produced 248,600 short tons of the above
pigments, paints, and pastes, against 53,300 " " imported.

What proportion of these amounts were really applied for the preservation of metallic structures on shore or afloat, it is difficult to determine; but one-fourth part may be taken as the yearly allowance to cover the effects of corrosion in progress in some degree in about every metallic structure that meets the eye, and may be considered as the annual contribution to the coffers of corrosion.

The general tenor of paint-trade literature would lead the layman to infer that each one of the above noted 420 firms was the right and only one that could or did furnish the special and imperishable paint that he was in search of. The customer who is in search of facts as well as paint will find some of the former in Chapters V, XXXII, XXXIII, XXXIV, XXXV that may guide him in selecting the latter.

The greater part of the mixed pastes and paints of the day are adulterations, and are presented to the public in these forms the better to conceal the actual composition of the pigments and to save oil; also to disguise the quality of the vehicle, as in the form of a paste or paint it requires chemical skill and time to analyze a sample of either. This, while applying in general to the mixed-paint house colors, does not exempt large quantities of mixed paints sold exclusively as ferric protective coatings.

There are at the present day as pure brands of linseed-oil, red and white lead, lampblack, and other pigments manufactured as any ever made. Possibly they are better on the average than those made one hundred years ago; but there are more that are a great deal poorer, and rendered more so by adulterations of the most barefaced character. There is a great advantage in the use of prepared paste, as the quality of the vehicle required to bring it to paint can be positively known, also the driers used, and what amount of these is necessary to meet any condition present at the time and place of applying the coating,—details that in most cases cannot be known in advance or by the paint-compounder, unless, as is too often the case, he makes but one kind, and fits it for the contemplated duty by the difference in price and the gullibility of the customer.

There are many reputable and responsible manufacturers of, and dealers in mixed paints, who will and do give a statement of the materials they use in a brand of mixed paint and the reason therefor. But they do not sell pure linseed-oil, under a fancy trade-mark, for 19 cents a gallon, nor a paint for 40 cents a gallon, that if the given materials were only approximately pure, would cost nearer a dollar. Neither do they expect it to be spread with a stiff, hard brush to enable it to cover a large area as a recommendation for its cheapness and superiority.

It costs as much for labor, brushes, scaffolds, and other items to spread a poor paint as a good one. On railway bridges, viaducts, and structural ironwork painted *in situ,* it costs for the painters' labor about twice the cost of the paint and in many cases four times as much,—depending upon the character and amount of scaffolds or ladder-work.

This assumes that a reliable paint is used that costs about a dollar a gallon, that will cover from 300 to 400 square feet of surface for the first coat, and from 500 to 600 square feet for the second or a repainting coat. In the latter case the surface covered may be less, or the same as for the first coat, all depending upon the labor of scraping or the condition of the surface of the old coating, whether scraped or not. Obviously, the claim that a paint can coat 1000 square feet of surface or more, and prove as durable as those covering less surface, as above, is not sustained in practice, though it is always possible to get a doctored result with any paint, good or bad. Paint-films—that is, the oil covering the atoms of the pigment—are only from $\frac{1}{500}$ to $\frac{1}{1000}$ inch in thickness, whatever the size of the pigment-atoms. It stands to reason that a thick coating of the vehicle will better protect the pigment-atom than a thin one. If the pigment-atom is susceptible in any degree to atmospheric influences, it will be less affected with a heavy coating of the vehicle than with a thin one. A thin coating usually implies that the oil has been reduced in density to render it easier to spread, and to be spread over a larger area, by the use of a larger quantity of solvents, either turpentine or benzine, than is necessary with any good quality of either raw or boiled linseed-oil.

Red-lead paint, from the large amount of oil in it and its great specific gravity, spreads over a large area, and it is these features that cause it to run or crawl on vertical or slightly inclined surfaces, particularly in the first coat.

A like result follows the use of *flake-graphite* pigments. The atoms of this variety of graphite, on account of their smooth surface and low coefficient of friction, appear to slide around in the vehicle before it dries enough to retain them in position when spread. The silica and barytes frequently mixed with such pigments to give a frictional resistance to overcome this gliding are almost as non-absorbent or repellent of the oil as the flake-graphite atom, and have a greater specific gravity to crowd them downward.

While the following excerpts * and the author's views are in the main more applicable to railway bridges and structural ironwork than to house-painting or the many minor ferric or composite surfaces that require painting, possibly, more for appearance than protection from corrosion, yet it is quite apparent that there is too much poor paint spread in both cases. The frequent failures or inferior results of all kinds of paint applied to all classes of structures can be attributed to, not only the paint and the manner and time of applying it, but to the improper preparation of the surface to be covered.

This is particularly the case in regard to bridge and structural painting. Particular emphasis is laid upon this point by every authority and writer on the subject in the technical literature of the master painters and engineering associations' debates and reports. Every specification for painting, bristles with clauses prescribing what shall or shall not be done, and still the fact remains that there are more failures than even indifferent successes, especially on work painted at the shops before shipment. The causes for the irregular and indifferent results are not difficult to ascertain. They are the improper application of the paint to dirty, greasy, moist or chilled, rusty or mill-scaled surfaces. No marked improvement in these uncertain results can be had until the same importance is attached to the "paint question," not only on paper, but in the actual supervision of the painting in all of its stages, as is given to the minutest construction details.

How carelessly this essential is generally performed even by engineers in charge of large bridges and other structures is seen in the instance of an inspecting engineer who reports visiting the workshops to observe the condition of the metal after being manufactured into structural work and during the painting process. "The metal had been housed, but there were many rust-spots on the web-plates, also on the angles, which were covered with scale. The metal was being cleaned by *putty knives and whisk-brooms.* Steel brushes were sometimes used (presumably as long as the visitor was present). *If there was anything unusual in this method of cleaning at the shops it was on the part of thoroughness.* (The italics are the author's.) After

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* Excerpts from *Engineering News,* June 6, 1895.

cleaning, the plates still showed thin yellow rust-spots, that showed plainly, but of a darker color after coating with oil. The oil was scraped from some rust-spots under the oil on dry girders in the yard, and the yellow color of rust, so often found, was developed."

It is to be regretted that this engineer's views of what constitutes a thorough preparation of the ferric surface for its coat of paint is not an exception, but the rule in more than nine-tenths of the structural manufacturing establishments. Notwithstanding their claims to pre-eminence in their profession, they have yet to learn how to protect what they create; and that they are either incapable of this, or indifferent to it, the present condition of the ferric structures of the day is an unanswerable evidence.

If the superiors do not understand the importance of the proper preparation of the surface to be covered, or the character of the paint and manner of applying it, or give them the same or more consideration than they attach to other matters of construction, it will be next to impossible for the inspector or master painter to enforce good work. It requires a more determined stand on the part of those in charge of this branch to ensure good work, than in any other part of the construction details. Until the head officers are zealous enough to care something about the condition of the work after it has left the shop, and the men actually in charge of the painting are given to understand that they will have the unquestionable backing and support of their superiors in any stand they take against the present so-called practical methods of structural painting by unscrupulous contractors, just so long will their work show their neglect in the rapid progress of corrosion, that will not need scraping the surface of the coating to find.

The low grade of labor available for the painters' gang has much to do with the generally unsatisfactory results obtained. Painting can be slighted and still present a creditable surface that will pass inspection more easily than any other branch of hand labor connected with bridge or structural ironwork. Painting is as hard in muscular requirements as light blacksmithing or the vise-work of a machinist, and the painter is not addicted to wasting his elbow-grease to work out his paint over any larger area than he can well avoid. In contract painting this element is noticeable, as there will often be 25 to 30 per cent of difference in the areas coated by different workmen upon the same job, and the eye can hardly detect the difference. The regular bridge inspector in charge of the work at the shop is so crowded with miscellaneous duties, that the inspection of the painting is usually a farce, even if the quality of the paint, the weather, and other conditions are favorable to secure a first-class result.

These features are particularly apparent if red lead is the paint used for the shop coat, as any want of care in keeping it continually well stirred up in the paint-pot by the paddle-stick (not by the brush) to prevent its "setting" is almost undetectable, and the want of care here governs the durability of all of the subsequent coatings. The use of lampblack with red lead in a paint coating, while it delays the quick "setting" of the coating, does not prevent the rapid settling of the pigment.

Probably the best results could be obtained if the man or firm who pays for the completed structural work appointed his or their own inspector to attend to this branch of the work with the distinct understanding that his orders were to be strictly enforced, and that his endorsement on the bill rendered was necessary before payment of the same. This would ensure the proper preparation of the surface, and secure careful attention to the before-mentioned necessaries; and he alone could be held responsible for the final results. In general, railway bridges that have the several coatings of paint applied under the direct supervision of one of the railway company's own corps of engineers have proven to be better protected against corrosion than the structures painted either by contract or by the most prominent of the construction firms, who, as a rule, are more anxious to get the work out of the shop, than for its future fate.

The pickling of structural iron with dilute acids to remove the mill-scale, as done in some classes of ship and boiler work, has met with many objections. These objections are primarily the cost of the process compared with a rush coat of something denominated paint.

When pickled and brushed clean of scale, the metal *must be* copiously washed in water and then dried if possible in the sun, or artificially in a warm room or oven, and then, whether machined or not, be coated with the first coat of paint. If a few hours elapse before applying the coating, the surfaces will begin to acquire the thin blush coating of red rust, as described in Chapter III.

The use of the sand-blast at the final stage of the machining processes will effectually remove the dirt and scale, but the machine-grease must be soaked free with turpentine and *thoroughly* wiped off, and not allowed to dry down again.

Both the pickling and sand-blast processes cost money, patience, and grim determination to apply, but the result in having a properly cleaned surface for the foundation of the protective coatings has been proven in hundreds of cases as the only sure method to reduce the maintenance expense of the structure. (See Chapter XXVIII, Sand-blast and Pickling.)

Many engineers are advocating the plan of having a coating of either boiled oil or paint applied to the iron or steel at the mill as soon as possible after it has left the rolls or hammer, and while the metal is hot. The hot part is the only part to commend. All metal as it leaves the rolls or hammer has a tough, thick or thin (as the case may be) coat of loose or partly loose scale that adheres for the time being, but on a short exposure to the air with a few changes in temperature, due to mill or storehouse conditions, releases its tension and is ready to fall off whenever handled, as in the course of loading and transportation. No amount of brushing that any mill employé would or could give to the metal in its hot or half-cold condition would remove this scale, and if the painter was present with his pot of oil or paint, it would get on over scales and all, and no ordinary inspector could prevent it, or be in any way sure that the contract requirements had been complied with in regard to the removal of the scale or the composition of the coating.

The mill coating is exposed during its application and drying to all the dirt, cinders, and sulphurous gases of the mill, which are a fruitful cause of decay in a dried coating of paint, and find an easier field in the green one. The mill-coated work is not allowed time to dry before being loaded for transportation, which adds its quota of dirt and cinders to the sticky paint.

All the subsequent machine operations are accompanied by more or less lubrication of the tool, and the oil used for this purpose is the cheapest to be had, and in general has been used over and over again; is dirty, sour, and more or less decomposed, and carries enough hydrocarbon to evaporate and dry down as a dirty surface skin, hard to distinguish from the coating applied at the mill. The sequence is that the inspector crowded to get the work out of the shop, and if at all careless in the discharge of his duty, does not personally see that the scales, dirt, and machine-grease are properly removed. The painter, anxious to show a great day's labor, and as a class prone to scrimping everything that calls for any manual effort other than with his brush, and jealous of any attempt to confine him to a procedure at variance with what he thinks is a special function of his craft, hastens to get on the paint, and takes more credit to himself in being able to *beat* the inspector than to do a meritorious piece of work.

Rather let the material go from the mill or forge to the storeroom or construction shop, protected as far as possible from any unnecessary exposure to the elements. When machined, during which process the greater part of the mill-scale will be loosened up so as to be readily removed, and when the several parts are assembled in their relative positions ready to be riveted up for their permanent places in the structure, if it is to be done at the shop instead of *in situ; then and there* is the place for the inspector to determine if the several parts are not only properly machined, but also properly cleaned from the scale that has not been removed by the machining and handling. He should see that grease, dirt, and any remaining scale, tight or loose, is removed in his presence, and the first coat of the paint applied in a manner to meet the atmospheric conditions at the time, and use a quality of paint that will ensure more than a guess at the future protective result.

Nothing can then serve as a cloak to hide the inspector's responsibility for the result. One inspector, and one inspection at the final stage, is better than a number of inspectors and inspections strung over a chain of operations comprising months of time and hundreds of miles between the links.

Many engineers advocate the use of boiled oil alone for the first or priming coat, applied either at the rolling-mill to protect the metal during its transit from the mill to the construction shop, or at the shop when ready to ship for erection. The general reason assigned for this practice is, that the boiled oil "*soaks into the scale* and dries and prevents further tendency towards corrosion."

This theory is *absolutely* without proof, from any standpoint. How far any oil or liquid can soak into iron or steel or the still harder mill-scale that forms on these metals, these Solons do not state. The use of such oil coatings is, in general, *to conceal* some slop-work on the part of the inspector, or constructor, at an earlier stage of the work than would be possible later on. However consistent and beneficial the first coating of oil may be for a wood or masonry surface, it has no part or parcel on a metallic one, when applied for the correction of the mill-scale evil. No number of these oil or even paint coatings will soak into and bond these scales together, or to the metal surface. There are hundreds of records of the painting of important railway structures, where the first coat of boiled-oil method was used, and, in the great majority of instances, the utter and rapid failure of the coating, and the extra corrosion of the structure, could be directly assigned to this so-called method of protection.

The weather-resisting power of an oil coating is almost *nil* compared with a paint, as before referred to in Dr. Dudley's experiments (Chapter I). If the advocates of oil coatings are so sure of its benefits as against a paint, why not make all the coatings of oil alone, no matter what it covers, a wire or an anchor? It will soak as far into one as the other. A paint coating can be applied as quickly and easily to any surface as an oil coat; will dry as quickly and as hard, and is in every way a better resistant to atmospheric or mechanical injuries.

A foundation coat of oil is a direct cause of the blistering and peeling of the coatings spread over it. It is seldom dried enough before the other paints are spread over it, to ensure a close adherence to the metal it covers. When the subsequent coats of paint are spread, the solvents and oils in them soften to some extent the underlying coat of oil, and a moderate heat from the sun causes the whole coating to blister or peel. Too much oil in a paint coating, particularly if the surplus oil is in or near the foundation coat, whether on a wooden or metallic surface, will generally cause peeling regardless of the pigment used in the coatings.

CHAPTER III.

IRON.

Symbol, FE. Atomic weight, 56. Specific gravity, 7.77.

Iron is never found pure in nature. Its avidity for oxygen is so great that it quickly forms ferrous oxide, FeO, or the protoxide of iron. This also is never found free, and is difficult to obtain chemically pure, its affinity for oxygen forming the sesquioxide—Fe_2O_3—called also the peroxide (the highest form of oxide for any metal) in which two atoms of iron and three of oxygen are united, or 70 per cent of iron and 30 per cent of oxygen.

In the latter form it is commercially known as iron oxide or iron ore, and is found in all parts of the world in all stages of purity, and in combination with the oxide of all the other metals in all proportions. The color of the protoxide is a green hue changing to a red-brown—that of the peroxide is a blood-red.

An intermediate oxide—the black magnetic, Fe_3O_4, three atoms of iron and four of oxygen = 72.4137 per cent of iron and 27.5863 per cent of oxygen—is the purest oxide of iron.

The ferric anhydride, FeO_3, is not known in nature, but is supposed to be formed by fusing iron or its oxide with nitre. Its color is a deep crimson.

Iron at a temperature of 230° C. (446° F.) combines freely with the atmospheric oxygen, becoming first covered with an extremely thin film of magnetic oxide, Fe_3O_4, of a light yellow color, which gradually passes into red, blue, and gray color. At a white heat, iron burns in the air with a production of magnetic oxide, the combustion being sustained for some time by directing a blast of air upon the heated metal. At a temperature of 360° C. (680° F.), iron decomposes steam, forming the black magnetic oxide of iron, Fe_3O_4 (the Bower-Barff coating), and liberating hydrogen.

Crocus, a fine powder formed when iron-scrap, borings, or ore are placed in contact with malleable- or cast-iron articles in a closed receptacle, and all brought to a red heat for the purpose of annealing them, is anhydrous iron oxide, Fe_2O_3, of a dull red-brown color. It is no better when used for a pigment than any natural iron ore, other than in its freedom from sulphur. It hydrates on exposure to the air or moisture to $Fe_2O_3+H_2O$, and can be reduced to metallic iron the same as any iron ore.

The precipitate formed from metallic iron when corroded under water is the sesquioxide or peroxide of iron, Fe_2O_3, plus three parts or 24 per cent of water, and is red rust, $Fe_2O_3+3H_2O$. It is a dull reddish-brown color, nearly a pure oxide, containing only such other metallic oxides as the iron contained from which it was corroded. It is comparatively free from sulphur, more so than the best hematite ore.

Oxides of Iron.

If purity of an iron-oxide pigment is any factor to prevent corrosion, these pure oxides ought to be better than any iron-oxide ores; but they are not, and plainly show that the failure of all iron oxide-pigments to prevent corrosion on a ferric body, or to add any resistance to the decay of the paint coating, lies in the natural inadequacy of a ferric pigment to resist its own inherent weakness, namely, conveying excessive amounts of oxygen with a tendency to excite electrolytic action.

Experiments determine that bright iron placed in an atmosphere of dry oxygen, or of dry carbonic acid, will not rust; when put in a damp atmosphere of oxygen, it rusted slightly; in a damp atmosphere of carbonic acid, a small quantity of white carbonate of iron is formed on the surface of the bright metal, but no rusting takes place. When, however, bright iron is placed in a *damp mixture* of the two gases—oxygen and carbonic acid—it is rapidly oxidized into copious excrescences of red rust.

In the opposite direction, to prevent rusting, a strong solution of carbonate of soda preserved needles and steel instruments, bright and untarnished, after thirty years of exposure, and would probably do so forever

Bright steel or iron objects remain untarnished in an atmosphere of dry muriate of lime, also in the dry carbonate of lime. Iron *immersed* in lime-water, caustic potash, and caustic soda does not rust; though the lyes absorb carbonic acid, they do not absorb oxygen.

The solutions of chloride of soda, kalium, magnesium, and ammonium quicken the formation of rust the same as dilute solutions of acids, if free oxygen has access. Under atmospheric influences that oxidize zinc, lead, and copper, the layer of the oxide formed is measurably thick and prevents any further oxidation. On the contrary, iron-rust once formed on a ferric surface never ceases its action so long as it is in contact with it. Rust produces rust.

The blush of oxide that appears upon the surface of a piece of bright, clean iron, such as is left from the action of the sand-blast or of a grindstone. forming after a few hours of atmospheric exposure and can be wiped off by the hand; or the piece of red rust from the iron-scrap heap; or the scales from the bottom or frame of an iron ship; one and all are the peroxide of iron, Fe_2O_3, plus three parts or 24 per cent of water. When calcined to drive off the water, they become precisely the same ferric oxide contained in any iron ore, and will reduce to metallic iron or grind to a pigment the same as any iron ore, however they may be designated or juggled with trade-names.

Fig. 4.—Rust produced on a clean rolled-iron plate exposed to atmospheric influences for 20 days. (Andes.)

In the corrosion of iron from any cause, for every 8 grains in weight gained by the iron, 46 cubic inches of hydrogen weighing 1 grain are set free. With each ounce of gain in the weight of the iron, 2515.625 cubic inches of hydrogen (=1.4558 cubic feet) are evolved, weighing $\frac{1}{8}$ ounce. Every pound of the oxide of iron requires the evaporation and dissociation of .29628 of a pound of water, representing the energy of about 1 pound of coal.

The magnetic oxide of iron is the richest of the iron ores in metallic iron = 72.414 per cent. It is non-corrosive, and, in the form of black titaniferous sand, found on the seacoast in many parts of the world, exposed to sea-water and other sources of oxidation and friction, has remained unchanged for thousands of years. Its use for a pigment is not satisfactory, on account of its black color and the difficulty of grinding it.

Specular iron ore is also but little affected by oxidation, and is a nearer approach to a definite compound of iron and carbon than any other known ferric substance: iron, 94.85 per cent; carbon, combined and graphitic, 3.50 per cent; silica, manganese, sulphur, and phosphorus, 1.65 per cent. It is an anhydrous ferric oxide, found in Nova Scotia, in the Isle of Sicily, and other parts of Europe, where mines of it have been worked for 3000 years. Its black color and hardness prevent its use as a pigment, though its resistance to corrosion is almost equal to that of the Bower-Barff surface.

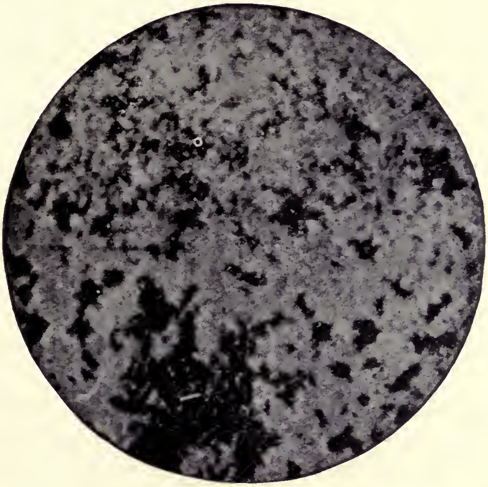

Fig. 5.—Rusting of a clean rolled-iron plate from a single application of water and left to dry. (Andes.)

The clay-iron ores from the coal measures, the spathic, bog, and many other iron ores, contain a very small amount of iron, and so large an amount of silica and other mineral substances that they are too refractory for smelting. They are not used for pigments for the same reasons that attend the magnetic and specular ores.

Hematite Ores.

The red and brown hematite-iron ores, composed of the sesquioxide of iron—70 per cent metallic iron and 30 per cent oxygen, plus water, plus variable percentages of mineral substances, plus carbonic, sulphuric, and phosphoric acids (see following analyses)—are the principal metallurgical iron ores, also those used for the production of pigments under the name of iron oxides, Fe_2O_3. This chemical symbol, name, and product is subject to more commercial jugglery to meet trade requirements than any other pigment in use. It is made to cover all sorts of combinations diverse in composition and character, supplemented still further by quantities of so-called inert bodies, more unstable than those in the ore with which they have been brought into forced relation.

These hydrated ores when calcined to expel the moisture—sulphuric, phosphoric, carbonic, and other erroneously supposed easily evaporated acids—become the anhydrous or supposed neutral, Fe_2O_3, plus about 2 per cent of water in a combined form, plus the acid elements that frequently amount to 2 per cent. Only 30 to 50 per cent of the sulphuric and phosphoric acids are dispersed in the comparatively low heat of the roasting process, and are not wholly consumed in the high heat of the blast-furnace, as manufacturers of metallic iron find to their annoyance.

The lime, magnesia, alumina, silica, manganese, and other oxides, whether in a combined state in the ore, or as added free substances at the time of roasting by calcination, become caustic and hygroscopic, and when ground to a pigment form, absorb moisture from the atmosphere, slack, changing their character again more or less to a flocculent or a powdered state. They do not bond in the slightest degree to the oxide of iron or base, are no more connected with it or to each other—except in a haphazard arrangement of their disrupted, separate natures—than the same substances would be if collected from a sand-bank.

No mechanical process connected with their incorporation into a pigment or paint can arrange them in sequence, or in any order where either substance can be supposed to protect its neighbor or even itself from any disturbing cause. Their excited, unstable condition and close association in a finely powdered form in the paint, render them only the more susceptible to catalytic action among the several substances of the pigment. This action soon destroys the weakest of them by electrolysis, set in action by their association as positive and negative electrical elements, or by the catalytic power of nearly all finely powdered substances to condense moisture and gases from the atmosphere, which the porous nature of the paint coating readily absorbs. If sulphur is present in either the pigment or vehicle in any recognizable quantity (as it nearly always is), it furnishes an additional excitant for the electrolytic action. This electrolytic action is further intensified by the unequal composition of all iron ores, whether roasted or not. The process of roasting—always an uncertain one—does not affect the ore equally. Lumps improperly roasted, or from their composition affected differently by the process, are difficult to detect in the hasty and generally poor assorting or picking-over the ore receives before pulverizing. The same uncertainty in the composition and assorting attends the unroasted ores.

In the pulverizing process there are many larger and harder particles of the ore that would not pass a No. 50 mesh sieve, if the pigment were bolted (as it seldom is), and would much less pass a 100 mesh, to which size all pigments should be reduced.

The finer the pigment the more thoroughly will it incorporate with the vehicle and protect itself and the surface covered. The destruction of any particle of the pigment will not render the coating so porous as when a larger atom is removed to permit access for the atmospheric moisture and gases. These lumps act as centres to determine the corrosive action, and in a measure explain the erratic action of all iron-oxide coatings. In nearly all rust-spots, one or more of these hard particles will be found, and particularly so wherever pitting has commenced.

The brown hematite ores are claimed to be practically free from sulphur, therefore the best for a pigment; but the best brands of this variety of ore prepared by any one of the many manufacturers of unroasted iron-oxide pigments have not proved to be in the slightest degree any more reliable in composition, or any better protection against corrosion—whether used as a straight paint or mixed with adulterants—than those prepared from the red hematites. (See following analyses of both pigments as used in commercial paints.)

The dirty purplish-brown or lifeless color of the brown hematites, even when freshly applied and aided by the gloss of oil, is not agreeable to the eye. Their ability to carry a large amount of uncombined substances, as inert pigments which add no quality to the paint as a protective agent, and the low cost of the whole line of iron-oxide pigments, are the great inducements for their production and use for ferric coatings.

ANALYSES OF IRON ORES.

By Various Analysts.

(Specific gravity from 5.33 to 4.85.)

	Brown Hematite (Limonite), 24 Different Ores (Hydrated).		Red Hematite, 8 Different Ores (Anhydrous).	
	Percentages.	Av'ges.	Percentages.	Av'ges.
Ferric oxide from...	90.05 to 32.76	59.54	98.71 to 66.55	89.13
Ferrous " " ...	traces " 10.54	1.22	traces " 1.13	00.16
Manganous " " ...	3.06 " 0.05	0.87	1.13 " 0.10	0.31
Alumina " " ...	27.95 " 0.05	4.48	2.79 " 0.06	0.82
Lime " " ...	0.06 " 27.72	4.20	9.40 " 0.37	1.97
Magnesia " " ...	0.17 " 10.21	1.30	1.39 " 0.08	0.42
Silica " " ...	63.52 " 0.79	13.90	8.90 " 1.00	5.77
Carbonic acid " ...	0.16 " 18.45	3.83	5.73 " 0.78	1.35
Phosphoric " " ...	0.06 " 3.17	0.63	1.02 " traces	traces
Sulphuric " " ...	traces " 0.28	0.03	1.31 " "	"
Iron pyrites " ...	" " 0.30	0.03	traces	"
Water combined and hygroscopic	18.60 " 6.60	10.25	2.12 " "	"
Percentages of metallic iron	63.04 to 24.09	42.45	66.10 to 47.47	62.37
11 samples averaged.......	52.65 per cent of iron.		Only one sample was below 66 per cent of iron.	
13 " "	33.81 " " " "			

There is a wide difference among these comparatively few and better quality ores, selected from many hundreds of ore-beds, on account of their purity and high percentage of metallic iron.

Many other mines furnish ores that are worked for the other metallic and chemical substances they contain, as nearly all the other metals are found associated with iron. All iron mines are noted for the variable quality of the ore taken from the same or from the adjoining bed, or from different parts of the same vein in each mine. The hematites are not exempt from this feature, whether used metallurgically or for pigments.

Though an analysis may show an iron ore to be good for metallurgical purposes it does not follow that such an ore is suitable for a pigment, however much the hematites may be desired as such, on account of their supposed freedom from sulphur or ease in grinding them unroasted.

Ores containing 40 to 60 per cent of the sesquioxide of iron and 30 to 50 per cent of silica have not proved to be any better protection against corrosion than those containing 80 to 95 per cent of the sesquioxide. This will be apparent by reference to the composition of the iron-oxide pigments given in the tests of commercial paints, Chapter XXX.

Iron-oxide Pigments.

The red hematites furnish a brighter-colored oxide than the brown hematites, whether roasted or not. The small amount of sulphur in the red ore develops in the process of roasting the dull-red color into a brighter red, simulating the Venetian and Indian reds so desirable to produce, but not always possible to get without doctoring the furnace product subsequently with substances more complex and unstable than the iron oxide itself. (See inert pigments, Chapter XVIII.)

The roasting process is a sensitive one. A few degrees of higher or lower temperature, or a little difference in the period of exposing the ore to it, or in the manner of cooling down the furnace, cause a great range in the color. The more sulphur in the ore the brighter the color.

There are from 10 to 20 per cent of moisture and carbonic acid in all iron ores as they come from the mines. If these are not driven off by roasting, they will not be dissipated in the pulverizing, and will be carried by the pigment into the mixed paint to its detriment. The use of an uncalcined iron-ore pigment is a long step toward an early corrosion of the ferric body over which it is spread.

The following analysis of an iron-oxide pigment made from a special red hematite roasted ore, one of the oldest and best known of this class of pigments, and the use of which as a special brand is probably greater than all of the other brands of iron-oxide pigments in the world, is of interest for comparison with an unroasted ore pigment:

MANUFACTURERS' ANALYSIS.

Peroxide of iron. (Equivalent in metallic iron, 36.477 per cent.)	52.11 per cent.
Silica combined	46.03 " "
Lime	0.23 " "
Moisture	1.59 " "
Loss	0.04 " "
	100.00 " "

Certainly, this is a pigment that should show a good result on either wood or iron surfaces, if there is any protective value in iron oxide. However, notwithstanding its almost uncontested use for over thirty years, on account of its low cost, agreeable color, and much lauded protective virtues, it proved so unsatisfactory for both wood and iron coatings that various railway companies—the largest consumers of paints—have reduced the 50 per cent of this peroxide of iron admissible in their mixed-color paints to 25 per cent. But this change has not resulted in any marked improvement in the protective qualities of the paint when applied to ferric bodies, nor are better results apparent upon wooden surfaces.

The following analysis is of a brown hematite *unroasted* iron ore. With a number of other brands of similar composition, it has been largely used by construction and railway engineers upon hundreds of the most important ferric structures in the country, whose serious corrosion, after but a short period of exposure, led to a special examination and report on their condition to the engineering firms responsible for their erection and condition:

Peroxide of iron (Equivalent in metallic iron, 65.128 per cent.)	93.04	per cent.
Silica combined	3.28	" "
Alumina combined	2.385	" "
Lime and magnesia	0.66	" "
Organic and volatile	0.42	" "
Sulphuric acid	0.03	" "
Moisture and loss	0.185	" "
	100.00	" "

This is a high-grade metallic iron ore comparatively free from sulphur, and whose merit as an anti-corrosive pigment was greatly commended (by the manufacturers) for a straight paint free from the usual class of inert adulterants. But its protective results as detailed in the said report were not better than the other adulterated oxide pigments, or the other coatings of mixed or unknown composition.

The following is an analysis of an iron-oxide pigment that is reported to have given very good results, being among the best of that class of compounded iron-oxide paints: *

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* Messrs. Hunt & Clapp, chemists and bridge inspectors, Philadelphia and Pittsburg.

Iron oxide	26.72	per cent	=to 18.70 per cent of metallic iron.
Carbonate of lime	30.19	" "	
Sulphate of lime	14.05	" "	
Clay and silica	19.90	" "	
Alumina	8.18	" "	
Magnesia	0.52	" "	
Water and organic matter	0.44	" "	
	100.00	" "	

Additional examples of iron-oxide paints and their erratic action—both mixed and straight pigments—will be found in the article on paint tests, Chapter XXX.

It is claimed that iron-oxide pigments, being the peroxide of iron, are incapable of further oxidation, and when ground with the vehicle are indestructible, and their capacity to condense atmospheric moisture and gases ceases. This is true as long as the thin film of the dried vehicle—only $\frac{1}{500}$ to $\frac{1}{1000}$ inch in thickness—remains in place on the external surface of the pigment atom, and no longer. The same causes that remove this film will affect the other part of the vehicle, in which the pigment atoms are imbedded. The vehicle, passive of itself to condense atmospheric moisture or gases, is porous and absorbent; and passes them on to the point where their decomposing action can take effect, if not on the iron-oxide atom, then upon the less resisting mineral substances associated with it as a pigment.

With the possible exception of silica and barytes, all of the so-called inert substances, usually mixed with iron-oxide pigments, are porous and absorbent of the vehicle and gases that reach them. The protection that these inert substances receive from the oil is no greater than the oil affords the iron-oxide atom, if not less, owing to the unreliable character of their composition naturally. If they have been mixed with the iron ore during the process of roasting, they are rendered more unstable, and readily pass to a lower plane of resistance, as mentioned before.

It may be questioned whether iron oxide is incapable of condensing moisture or gases. It induces and promotes oxidation in all organic bodies with which it is brought into contact, and is used in the process of boiling oil to increase the catalytic power of all siccative oils to absorb oxygen from the air. Its use with raw linseed and other oils is to absorb the glyceride element that, unabsorbed or unchanged, in all fatty oils delays the drying process, condensing the atmospheric moisture and gases that act below the external film of the drying oil, thus laying the foundation for a blister with subsequent corrosion of the coated surface.

The power of iron oxide to absorb the glyceride is about two-thirds that of red lead. If the iron-oxide atom is insensible to the presence of sulphur that may be presented to it in any form, the other associated mineral substances and vehicle are not, and a very small percentage of any acid will set in motion the electrolytic action so fatal to ferric substances.

As a class, the inert pigments are electro-positive to the iron-oxide atom, and are the first to be affected by any electrolytic action inaugurated by their presence in the paint.

The iron-oxide atoms are electro-negative to the ferric surface over which they are spread.

In iron-oxide and zinc-oxide mixtures, the iron atom is electro-negative to the zinc atoms, which are quickly destroyed. If any copper or copper oxide is present in an iron-oxide pigment, the iron oxide is electro-positive to the copper and is destroyed.

Mallet's experiments determined that copper and zinc in any form, added to, or in contact with iron in any form, increased the corrosion of a covered iron surface 60 per cent in a given time; copper, without the zinc element, 40 per cent.

The irregularity of the distribution of the atoms in a compound iron-oxide coating—their difference in size and character—determine the points of corrosion, which once established end only with the complete failure of the coating.

From five to ten per cent of the sulphate of lime ($CaOSO_3$) is generally found in iron-oxide paints or pigments. It is usually specified by the consumer that it shall be fully hydrated, or that it shall contain not more than one part of water. The effect of the moisture is to aid any sulphur element present to commence promptly its work of disintegrating the coating. From its great covering power, the ease of grinding and mixing it with the iron oxide, and its cheapness, one third of the weight of the pigment is frequently composed of this substance, particularly in the tint colors. The greater the amount of this sulphate of lime, the sooner the destruction of the coating.

The copperas oxides of iron stand remarkably well upon wooden surfaces. The brown oxides stand the best upon ferric bodies. The Venetian red oxide, from the old iron-oxide mines, had a peculiar preservative action on the surface of wood. Two or three coats from the pure materials have outlasted the record of their application and the lives of the painters that spread them. These oxides and white lead form a hard mastic covering, and unless spread over unseasoned or wet wooden surfaces, are not liable to blister or peel.

Many of the irreconcilable discrepancies in the use of iron-oxide paints can be attributed to the careless method of preparing them. In general practice, it is never ground with the oil, and but seldom machine-mixed. The dry pigment in the ratio of six to seven pounds and about the same weight of oil (or three-fourths of a gallon) are placed together in a tub, and after a few hours of soaking are simply stirred up and spread. If any large quantity of paint is so prepared, it is almost impossible to secure thorough incorporation of the pigment and the oil, owing to the different specific gravities of the several substances composing the pigment, which vary from 2.2 to 4.9. This manner of mixing is strongly recommended by the iron-oxide trade to secure its use, at the expense of the life and effectiveness of their product, which many times might be more creditable were better care taken to render it deserving.

The longer that iron-oxide paints are ground in the full quantity of oil they require to form a *paint*, the more lasting they will be, and this effect is equally apparent in all pigments.

The unsatisfactory results due to careless mixing are aggravated by the use of large flat brushes that act as mops to carry or slap on a large quantity of paint, inadequately, in this way, brushed out. Such brushes carry air into the coating, rendering it more porous in drying than it otherwise would be were heavy, long-bristle, round brushes employed. The same objections exist where the coating is applied by the air-brush or spray apparatus, only in a more marked degree. See Chapter XXXI.

There are many tests for the adulteration in iron-oxide pigments or paints of too extended detail to be entered into here. A ready test for the soluble sulphate of iron in an iron oxide is to warm a little with pure water and filter through blotting paper. Add to the clear solution a few drops of hydrochloric acid and a little of the chloride of barium (both obtainable at any drug store). If a white sediment forms in the solution, the sample of iron oxide should be rejected.

There are many recorded instances of the excellent results attending the use of iron-oxide pigments. Berzelius (1838) mentions that on houses in Sweden, painted with iron oxide three hundred years ago, the coating was still in fair condition, and the wood-work well preserved. The wooden houses and workshops in many parts of the United States bear testimony equally in favor of this class of paints, in the general good condition of the paint and structure after exposures, without repainting, of fifty to eighty years. But in every case the cause of these excellent and exceptional results was in the use of better materials and better methods of application than is the present-day practice.

Paint-trade literature frequently cites that the tin roof of Independence Hall in Philadelphia has been protected for the past one hundred and thirty years with an iron-oxide paint, giving this as an unanswerable argument for the protective character of these pigments applied to metal surfaces. The facts in this case show that the plates with which this particular roof was laid, as well as many others at that period, were double-coated with pure block tin, free from lead, zinc, or antimony, more scrupulous care being taken in every part of its manufacture to secure a reliable product, than is now practised by even the best of the present-day tin-plate manufacturers, whose products almost universally fail by the corrosion of the iron plate

FIG. 6.—Corrosion of the present-day make of tin plate after storage in a dry cellar for ten years. (Andes.)

on which the tin is coated. This internal corrosion casts off the tin, and no amount or kind of paint spread upon an inferior quality of tin-roofing metal can prevent this internal corrosion, though it may conceal its presence and progress, and possibly fill up some small holes in the early stages of the decay.

There are scores of tin roofs covering important buildings in the Canadian Provinces that have been laid for nearly a century, as bright and uncorroded now as when first laid, never having had a coat of paint to protect them.

Pure block tin is unaffected by atmospheric conditions, almost as much so as copper. It was only when poorly cleaned plates, poor tin for the coating, acid flux instead of resin for soldering, and careless methods of laying the roof generally, came into vogue, that we began to hear of the virtues and need of an iron-oxide paint to prevent the corrosion of a tin roof. Granted that a good quality of tin roofing is none the worse for a coating of paint applied a year or two after the roofing is laid, yet it is quite as essential for the future life of the roof that the paint should be also of good quality.

The original mines from which the iron-oxide pigments known as Indian and Venetian reds were taken have long been exhausted. These old mine pigments required no roasting or doctoring to develop their color, or to correct any acid elements in them. The reputation of these pioneer oxide pigments, like that of the "Old Dutch Process" white lead, has been assumed to reach and cover the advent of scores of substances bearing little resemblance to their progenitors, except in name, and even this is not exempt from the greed of some modern paint-compounders, as the many prefixes and trade-marks bear witness.

Fig. 7 shows the protective character of an iron-oxide paint applied to a railway viaduct not properly cleaned from mill-scale before painting, and when painted was exposed to combustion gases, cinders, dust, and moisture.

Prepared iron-oxide paints are often brightened by the use of aniline colors, but are not durable. Burning a sample of such paints over an alcohol lamp will destroy the aniline, and leave the iron oxide its natural color, exposing the cheat. The tendency of all iron-oxide paints is to darken with age, due to the natural darkening of the oil vehicle by age, rather than by change in the pigment. While nearly all of the iron-oxide paints are adulterated, barytes, chalk, sand, silica, and all added substances lessen the covering power. The clays also absorb water and hasten the decay of the paint.

FIG. 7.

Copperas Oxide.

The chemical composition of copperas is $Fe.SO_4.7H_2O$ = one part of iron plus one part sulphuric acid, plus seven parts of water.

Copperas, the waste product of many manufacturing processes, is largely used to produce an oxide-of-iron pigment by roasting the crystals. Six parts of the water are driven off by a heat of 114° F., but one atom is still retained at 280° F. At a red heat it decomposes, giving off one part of sulphurous oxide, leaving a basic ferric sulphate, $Fe_2O_33SO_3$; and, more strongly heated, it leaves a pure ferric oxide known as Colcothar vitriol.

As usually roasted for an iron-oxide pigment, from three to five pounds of terra alba, lime, or chalk, to one of the ore, are put in the roasting-furnace, heated to a high heat to expel the sulphur, which is supposed to combine with the lime, forming a synthetical sulphate of lime (gypsum). This combination is the same as in the roasting of iron ore with chalk or lime to remove the sulphur, and will be found in detail in the list of inert pigments under "Gypsum." The process is a sensitive one, the color of the product being the bright-red color pigments,—Venetian and Indian reds. Both colors are due to the degree of heat employed, the length of exposure to this heat, the manipulation, manner and time taken to cool the mass, etc.

All of the sulphur is not dissipated by the heat nor absorbed by the lime in its change from a carbonate to a sulphate. The lime changed to gypsum or left free, being in great excess of the amount that is allowable in any pigment, is removed to some extent by sifting, or other means, before grinding the furnace product.

Copperas oxide requires great care in its use, either by itself or mixed with the dead-color iron oxides or other pigments to bring up their color, as the sulphur goes into the paint with the usual results. No amount of free adulterants or inert substances have any material effect in neutralizing it.

Copperas ferric salt (a protosulphate of iron), Coquimbite, is found native as a hydrate, containing nine atoms of water, $Fe_2O_33SO_3 + 9H_2O$. It occurs in layers several feet thick in fine-grained six-sided pyramid crystals. Its preparation for a pigment is similar to that described above, and the resulting disintegrating effect in the paint is not measurably different.

Yellow Ochre.

Ochre is a hydrated oxide of iron of a strong yellow or brown-yellow color, generally containing less than 40 per cent of iron oxide. The ochres are among the oldest of pigments. Samples have been obtained from Pompeii in all stages of preparation from the ore to the mixed paint. They were used in Greece in the time of Pliny, and in Old Egypt. They are the most stable of the yellow colors, and are the principal pigment in the present freight-car colors.

Ochres are clays tinted with the oxide of iron and manganese, and hygroscopic in character, carrying from five to fifteen per cent of water. Dried artificially to expel the water, they change color to pink or red the same as all other iron-oxide substances.

Their yellow color is chiefly due to the iron oxide, and the more of this they contain the darker the color. The brown color is due to the manganese oxide. All ochres contain some amount of this oxide. The darker colors (unroasted) contain the most manganese, and are good driers for use with linseed-oil.

The covering power of the ochres depends upon the amount of lime or chalk in them, which reduces the coloring power by rendering them translucent. They require from sixty to eighty per cent of oil to form a paste, and the added quantity of oil to make them spread makes them slow driers. They blacken a little in time exposed to sunlight, but the change in tone is evidently more from the darkening of the oil than from a change in the pigment.

The best brands of ochre are the French:

Composed of clay	69.5	to 73.8	per cent.
Oxide of iron and manganese	23.5	" 25.6	"	"
Water	7.0	" 9.5	"	"

French ochre has a large spreading power, as it absorbs a large quantity of oil, and it holds well to wooden surfaces. It should be ground in raw linseed-oil, and if a thinner is required, raw oil should be used. White ochre has the property of holding well to wooden surfaces from the large amount of oil taken up by it, but does not bond well to any overlying coat of white lead, and tends to cast it off by peeling. This action can be avoided by using a small percentage of white lead in the priming ochre coat.

The English Oxford and stone ochres are among the best brands. The Roman ochres grade with the best Havre, while the lower grades of French ochres are poor and possibly lower in covering power than the best Bermuda (Virginia) or other American brands.

The name of an ochre signifies, like all other paint names, little, unless the material is furnished from a responsible business firm. Even these cheap earths have to bear a share in the general burden of adulteration that is the order of the day, by an added quantity of clay, chalk, and barytes (the latter to give weight), but all injure the covering power of the ochre. Their presence is usually denoted by the increased amount of oil required to bring the dry ochre to a paste.

There are many mixtures of ochre as the basic pigment for a ferric coating other than those classed as freight-car colors. One recommended by Dr. Dudley, and used to some extent upon the Pennsylvania Railroad, has decided superiority over the general brands of iron-oxide paints marketed under the many alluring and always misleading trade-names.

Dr. Dudley's formula is: French ochre, 39 lbs.; lampblack, 1 lb.; japan, as drier, 6 lbs.; raw linseed-oil, 54 lbs. (or $6\frac{3}{4}$ to 7 gallons, according to time of the year that the paint is to be spread). Hot weather requires the least oil.

The better brands of ochre as the basic pigment for freight-car colors form very durable paint coatings, whose life is generally equal to that of the car. The cheaper grades were formerly used to a great extent as cheap paints for tin roofs, but the large amount of free sand, lime, and other uncombined mineral substances, acids, and moisture that they contained, with the coarse way they were calcined and ground, rendered the coatings short-lived and unsatisfactory. They required a large amount of oil to spread them, even with a whitewash brush. They dried or hardened rigidly, did not bond to the tin, and the rate of expansion and contraction from the action of the sun was so materially different from the tin they covered that they soon cracked, blistered, and flaked off.

Umber.

Umber is an argillaceous brown hematite ore, essentially $2Fe_2O_3SiO_2H_2O$, with alumina and manganic acid. Specific gravity 2.2. Originally obtained from Umbria, Italy, now chiefly from Cyprus.

As a pigment it is used in both its raw or natural state, and when calcined is known as burnt umber. When calcined at a low heat it turns a dark brown; a stronger heat dehydrates it, turning it to a red brown and softening it. As a ferric paint it has no special quality other than the ochres. The cheapness of the pigment is more than offset by the amount of oil it requires for a good spreading paint.

Umber is used as a drier in boiling linseed-oil, and furnishes an oil of good color; but unless used in large quantities, does not make so rapid a drying oil as the lead, zinc, or manganese driers.

Spanish Brown.

Spanish brown, an iron oxide or ochre, containing thirty to fifty per cent of clay, is inferior in color and covering power to umber, but is of lasting value for a roofing paint, as the clay, which has at all times a strong affinity for moisture, will, when properly calcined, take up seventy to eighty per cent of oil, and this oil, protected from the sun and air, in turn protects the covered roofing metal thoroughly. On vertical surfaces, however, less oil must be used, else the coating will be liable to crawl before it is dry, and the ochre, not being so well protected as on the horizontal surface, will absorb moisture, soon corroding the ferric surface. If two or more ochre coatings are spread over one another, the last coating is *liable to peel;* hence, for tin or metal-covered roofs, one heavy coat is better than two or more thinner, unless the latter are applied after an interval of a year or more. The more elastic the first coating of this pigment, the more durable; but the greater will be the tendency to cast off or crack the second or other coats.

CHAPTER IV.

RED LEAD.

Metallic Lead. Symbol, Pb. Atomic Weight, 206.9.
Specific gravity, pure 11.445; commercial 11.335 to 11.388.

LEAD occupies an important part in the arts and manufactures of the day, and requires a greater range of chemical and mechanical processes for its production as a pigment and more care in preparing and applying it for a paint than any other pigment.

In its mineral form it is associated with all of the noble metals, also with copper, tin, zinc, bismuth, antimony, arsenic, etc. Some of the baser metals are always present in commercial pig lead, and affect the character of the pigments prepared from it by the processes of calcination, oxidation, sublimation, corrosion, and precipitation.

There are twenty ores of the metal known to the mineralogist, but metallic lead is produced from the five following minerals, the analyses of which indicate not only the character of the ore but also of the metallic lead and pigments made from them:

SULPHIDE OF LEAD, PbS (GALENA, BLUE-LEAD ORE).

Oxide of lead	81.80	to	85.13	per cent.
Oxide of silver	0.08	“	0.02	“ “
Oxide of zinc	3.59	“	2.18	“ “
Sulphuric acid	16.40	“	13.02	“ “

SULPHATE OF LEAD, $PbSO_4$ (ANGLESITE).

Oxide of lead	71.00	to	72.46	per cent.
Oxide of iron	1.00	“	0.09	“ “
Sulphuric acid	26.09	“	24.08	“ “
Water	0.51	“	2.00	“ “

CARBONATE OF LEAD, $PbCO_3$ (CERUSSITE).

Oxide of lead	66.00	to	84.76	per cent.
Oxide of iron	2.30	“	0.00	“ “
Oxide of alumina	15.30	“	0.00	“ “
Carbonic acid	13.00	“	16.49	“ “
Water	2.20	“	0.00	“ “

PHOSPHATE OF LEAD (PYROMORPHITE).

Lead (metallic)	7.80	to	7.39	per cent.
Oxide of lead	73.22	“	74.50	“ “
Phosphoric acid	15.76	“	15.94	“ “
Chlorin	2.67	“	2.54	“ “

ARSENATE OF LEAD (MIMETESITE).

Oxide of lead	74.96	per cent.
Arsenic acid	23.06	“ “
Chlorin	2.44	“ “

Metallic lead forms five oxides that in one or more forms are the result of the heat or chemical changes produced in the metal in converting it into a pigment. They are:

		Lead.	Oxygen.
The suboxide	Pb_2O	= 96.277 per cent.	3.723 per cent.
“ protoxide	$Pb.O$	= 92.822 “ “	7.178 “ “
“ red oxide (minium)	$Pb_3.O_4$	= 90.630 “ “	9.370 “ “
“ sesquioxide	$Pb_2.O_3$	= 89.606 “ “	10.394 “ “
“ dioxide or peroxide	$Pb.O_4$	= 76.375 “ “	23.627 “ “

Red Lead, or *Minium*, is the principal pigment produced from the oxides, its specific gravity being 8.5 to 8.94, depending upon the purity of the lead "Massicot" or litharge, from which it is made. The color also depends upon this point, but in a greater degree upon the temperature employed in the oxidation of the material, the uniformity of the heat, the manipulation of the material in the furnace, the length of time exposed to the heat, and the rate and manner of cooling down the furnace and its contents.

Special furnaces and processes are required in its preparation that differ materially in the various countries where red lead is produced, also in different manufactories, and there is a difference in the materials employed.

Briefly described, these processes are: First, by the cupellation furnace which converts metallic lead into litharge in about 24 hours. Second, a reverberatory furnace in which litharge is converted into red lead. Third, a reverberatory furnace or oven that reduces metallic lead into litharge. In any of these processes the litharge is the first product, and is always formed whenever metallic lead is heated to about 900° F. for about 24 hours and freely exposed to a current of air, the material being continuously stirred during the heating process. This crude product or litharge is a coarse granular substance that upon further heating is fused into a crystalline mass. When cold this mass when broken up is in the form of thin yellow or brown scales, and in this state is known as flake or glass-makers' litharge. This, when ground in water and dried, changes its color to a buff, and is the ordinary commercial litharge.

When the crude litharge powder is again moderately heated in a reverberatory furnace or oven and exposed to a current of air with continuous stirring for from 26 to 48 hours, or until a sample drawn at a low red heat appears of a dark-red color turning to a bright red on cooling, the furnace is closed and allowed to cool slowly; a condition most essential to success in the color, that if not satisfactory, requires a reheating and cooling of the product now known as red lead.

Red lead made from litharge (from the imperfect oxidation of the litharge) contains a larger amount of the protoxide of lead than that made from the carbonate or white lead, where, on account of the finer condition of the material, the oxidation is more complete, more quickly effected, and generally of a better color and quality.

With this complex chain of operations there are many trade secrets to secure not only a uniform quality of the pigment, but its color. The latter nearly always remains an uncertain element even with the best of attention given during the whole process.

Red lead is found native in many localities mixed with the other ores of lead, probably resulting from their oxidation by natural causes. Chromate of lead ($Pb.CrO_4$. Specific gravity, 4.6 to 5.2), the neutral, or meta-chromate, known as crocoisite or lehmanite, is a native red-lead ore found in commercial quantities in many parts of the world. It is in the form of translucent crystals of a yellow color with various shades of other colors, and is associated with decomposed gneiss and granite. The method of converting these red-lead ores into pigments need not be described here. All of the yellow and red chromates of lead are obtained from crocoisite. They are strong colors, and do not decompose on exposure to the air or light.

Red lead is one of the heaviest and most expensive pigments, also the most difficult to prepare for a paint or to spread. It is more susceptible to adulteration, and is more adulterated by interests inimical to its reputation, than any other pigment, with the possible exception of its sister-product, white lead. There are many well-authenticated instances of its perfect protection of important structures, and a great number of its failure in locations where the failure can be directly traceable to causes detrimental to the success of any pigment. It has been, and is, condemned for causes directly traceable to its improper preparation and application, and where the failure should have been foreseen by the engineer or master painter, and where carelessness, indifference, or ignorance of the conditions to which the coating was to be subjected, were the prime factors of its non-success.

When obtained from a reputable manufacturer and properly prepared with a suitable vehicle and spread under known conditions of its future service, it has proved to be one of the most reliable pigments. Its color is distinctive, hence it is not favorable to the use of adulterants. Brick-dust, iron oxide, and barytes tone down its high color, but are detrimental in all other respects. Chalk, gypsum, and other light-color and low-specific-gravity substances are often added to correct the tendency of red-lead paint to "set" in the paint-pot while applying it, or to prevent its "creep" when spread upon vertical or inclined surfaces. All such adulterants are easily detected; they do not prevent the set or crawl of the paint, and are the principal cause of the failure of the coating. For the foundation coat upon ferric bodies, it will cover about as much surface as any other paint applied under the same conditions and with the same effort on the part of the painter to brush it out. The latter factor is frequently too small to ensure success with even a whitewash.

As a first coat on ferric bodies, applied at the workshop, its color shows at once any material injury to the coating due to the usual handling and transportation, also readily indicates if the grease and dirt due to the machining processes in the shop or received during transportation and erection have been properly attended to or not. It is a prime watch-dog in this respect.

Its tendency to settle in the paint-pot, also "to set," and the necessity for constantly stirring it up by the painter, probably lessens by a small amount the number of square feet of surface he can spread in a day. This is probably an objection to its use, but is offset by the many points in its favor. The rapid set of red lead when mixed—a peculiarity of this pigment—is as objectionable in a paint before it is applied to the surface as the set or hardening of hydraulic cement on the mortar-board. When either the paint or mortar has set before being spread, it is useless for its intended purpose. If the set of either is broken up by stirring and they are then applied, both may appear to be of the same nature as before setting, but they are injured beyond recovery. The mortar will not be much better than a wetted sand,

and will not again bond the sand or to the masonry. The red lead will not recover its combining power that ensures the mutual bond between the atoms of the pigment and to the surface covered, be it wood or metal. When in this condition, if it is applied to a metallic surface, it "crawls," as it is called, and presents an appearance more like that of curdled milk than a paint, and the actual protection of the body covered is due to the vehicle only. It will add but little to the covering power other than what any adulterating substance would do.

The setting of red lead is due to two chemical reactions, namely, a combination between the litharge of the red lead and the glycerine element in the oil; also a combination between the fatty acids of the oil and the litharge, forming a lead soap, quite a firm substance, but one not favorable to the durability of the paint.

Many of the failures of red-lead coatings, if rigidly traced to their source, would no doubt be found to have been caused by the carelessness of the painter in not keeping the paint well stirred during its application, or in preparing too large a quantity for immediate use, or by using the paint left over from day to day, or from another job.

Red-lead and Lampblack Mixtures to Delay "Setting."

Iron oxide, zinc oxide, barytes, gypsum, etc., added to red lead to prevent "setting," are objectionable and ineffective, as before noted. Lampblack from $\frac{1}{4}$ to 1 ounce per pound of red lead delays the setting action and enables the red lead to be prepared as a paste to be used in the immediate future, when it is thinned by additional oil at the time and place of using. The bright red of the minium is modified by the lampblack to a chocolate color that may be light or dark according to the quantity of the lampblack used. Lampblack of itself is an excellent pigment, is electrically passive or neutral to all pigments, and by natural formation is so finely divided that it mixes easily and thoroughly with the oil and red lead without deteriorating the quality of either.

Many painters have reported a difficulty with the use of red lead and lampblack: that with 1 ounce of lampblack per pound of red lead the paint would not dry promptly for shop work without the use of japan or turpentine driers. Bridge engineers, however, report that red-lead paints carrying 10 ounces of lampblack to 12 pounds of red lead have stood for three or four months without setting or hardening by simply agitating or rolling the barrels daily. In one case the paint barrels were left undisturbed for four months, and though the red lead had settled in some degree, when it was stirred again the paint spread as well and dried as firmly as though freshly mixed.

Lampblack containing sulphur in any appreciable amount should never be mixed with red lead for a coating. Ground soot from chimneys or furnace-flues, ground bituminous coal or coke, or the soot from most of the petroleum or heavy mineral oils, contain sulphur enough to cause the prompt failure of a red-lead coating, even when used to the amount of $\frac{1}{4}$ of an ounce per pound of red lead.

Mr. Ball, master painter Pennsylvania Railroad, 1897, reported the result of some of his experiments with "protective paints for metallic parts of cars and trucks," viz.:

First. Red lead and raw linseed-oil, with litharge as a drier.
Second. Red lead and raw linseed-oil, no drier.
Third. Red lead and lampblack, equal parts.
Fourth. Red lead one part, lampblack three parts.
Fifth. Mineral brown (red oxide of iron).
Sixth. Mexican graphite.

All paints were mixed from the same quality of raw linseed-oil; none but the first had any drier.

At the end of fifteen months of atmospheric exposure at the car shops their condition was as follows:

Number One had failed in two or three spots.
" Two was intact and appeared to be in condition to resist a number of years' wear.
" Three had scaled off in a number of places, showing rust.
" Four was in a still worse condition.
" Five was completely gone.
" Six was in perfect condition, the same as the straight red-lead sample.

The slow setting and drying mixtures of red lead and lampblack are probably better for field work, where slow drying is of little moment, unless bad weather conditions are to be met, than for use at the shops where the transportation requirements govern. Thinning the red-lead and lampblack paste with boiled oil when the paint is applied will add the necessary drying element to the paint without the use of turpentine.

Spirits of turpentine is objectionable in all paints, as its evaporation leaves the coating more porous than it would be if the paint dried naturally; and it deadens the gloss. Japan driers for red-lead paints are less objectionable than the turpentine. They are heavier and add resinous matter to the paint in drying that is of the same character as the vehicle with which the red lead is ground. The drying of japan is principally by resinification and not wholly by evaporation, as is the case with turpentine; with the added japan the period of drying can be governed as required by using a small proportion of raw linseed-oil.

Excerpts from a trade catalogue * relative to the use of turpentine and red lead say: "We are not prepared to advise the use of turpentine in shipyards, where, owing to time contracts, it is often necessary to paint in damp or freezing weather, though the practice in the Marine Department of the Maryland Steel Co. from many years' experience in the use of red lead is, viz.: Use three parts of linseed-oil (raw, presumably) and one part of turpentine for the first and second coats, with sufficient drier (presumably japan) to set well in twenty-four hours, allowing five to six days between the coats. The third coat to be an oil coat without drier."

FIG. 8.—Dried film of red lead encrusted with rust × 100. Taken from a painted structure which showed no rust on surface. (M. Toch.)

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* "How to Use Red Lead." National Lead Company.

"Theoretically, and for dry, bright weather, red lead should be used with raw linseed-oil and no drier, red lead itself being a natural drier. By so doing, the chemical union between the pigment and oil is most complete and the resultant paint is more durable. However, for ordinary service add a small quantity of japan or use boiled linseed-oil. By so doing a more viscous vehicle is had, which better sustains the heavy particles of the red lead, thereby preventing its running on vertical surfaces, and possibly giving greater covering."

Red-lead Paint Mixtures.

Many railway engineers favor the following mixture of red-lead paint for their structures where the time of drying is of little moment. For the first or priming coat, 20 pounds of red lead and 1 gallon of raw linseed-oil. No driers. For the second and third coats: a paste made from 60 pounds of hydrated sulphate of lime, 30 pounds of lampblack, 5 pounds of red lead, making 100 pounds of pigments, to which 20 gallons of boiled linseed-oil are added, making 30 gallons of paint. This makes a fair drying paint of a dark or dirty grayish-brown color, weighing about 8¼ pounds per gallon. All of the power in this paint to prevent corrosion lies in the red lead and lampblack, the sulphate of lime adds the stuffing for quantity without contributing anything of a protective character to the mixture, and the covering power is poor.

If any of the low-carbon amorphous graphites were substituted for the sulphate of lime in this formula, the paint would be better in all respects for coating ferric bodies.

Mulder's Experiments with Cheap Red-lead Paints.

Mulder, in his experiments to produce a cheap paint, used boiled linseed-oil containing 2½ per cent of red lead. He used 100 parts of this oil with every one of the following mixtures. The iron oxide used was Cartier's (Belgium), that analyzed as follows:

Iron oxide	68.27	per cent	= 47.79 per cent of metallic iron.
Clay	27.00	" "	27.67 " " mineral substances.
Marl	0.27	" "	
Chalk	0.40	" "	
Water	2.75	" "	
Undetermined	1.31	" "	
	100.00	" "	

200 parts of pulverized fine sand, 5 parts red lead, gave a paint of some merit.

Red lead 25 per cent, iron oxide 40 per cent, gave a very good coating.

20, 40, 60, parts of red lead to 100 parts of iron oxide gave excellent results. 20 to 90 parts of red lead to 50 parts of pulverized red roofing tiles gave a thick heavy coating.

40 parts of red lead and 100 parts of pulverized red roofing tiles gave an excellent coating.

20 to 90 parts of red lead and 100 parts of pulverized ironstone gave a paint of distinguished excellence.

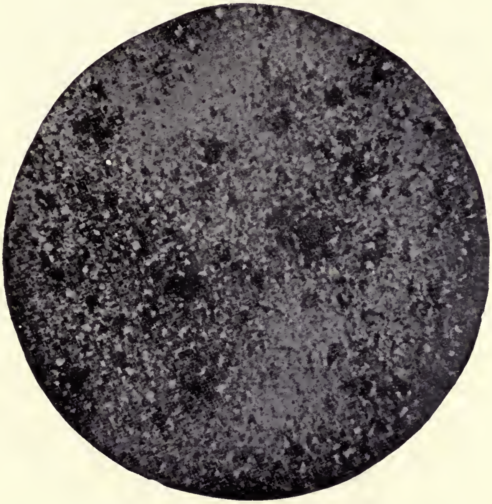

FIG. 9.—Photomicrograph×100 of a film of red-lead paint showing grains of various sizes, all more or less encysted with air-bubbles. (M. Toch.)

Other mixtures of red lead favorably reported upon by experimenters are red lead, zinc oxide, and Blanc-Fixe. The latter substance serves to hold up the red lead in the mixture during the first stage of drying and prevents its "creep." Amorphous graphite is also used instead of the Blanc-Fixe for the same purpose. None of these substances or any others employed for this purpose can be so mixed that they will not be subject to the influences that destroy all compounded paints, as mentioned elsewhere in this work. (See Chapters XXVII and XXXII.)

The bright lustre of red lead is often toned down by Venetian red. This pigment, if it could be obtained from a natural ore, is a very desirable one, but the mines that furnished it in former days have long been exhausted as a commercial source of supply, and the copperas reds have taken its place. These contain a large amount of sulphuric acid loosely held in combination (see Analysis, Chapter III), and their use with red lead is as disastrous to the paint as the direct effect of hydric sulphide.

The effect of the sulphur element in both cases is greatly influenced by heat, a few weeks' exposure to hot summer temperatures being all that is necessary to destroy the coating by rendering it brittle and easily removed by the hand, or else causing it to peel in strips. This action of the sulphur is sometimes said not to be due to a change for the worse in the red-lead atoms, but to the change in the vehicle. But the effect of sulphur upon dried linseed-oil is almost *nil*, and the oil-film is always nearly transparent of itself, whatever pigment may be associated with it. Any change in the pigment is denoted by a change of color in the paint, whatever may be the cause of the change. The change in the pigment simply shows through the thin film of dried oil quite as readily as though it were of glass, and generally indicates a speedy dissolution of the coating. In many mills and workshops all of these conditions—heat, sulphurous fumes, and saturated atmospheric elements—are present, and red-lead coatings in such locations are short-lived.

The sulphur element, whether in the oil or the red lead, or from any other source, renders the paint liable to dry on the surface only, and the inner portion of the oil that encloses the pigment-atoms remains soft and, therefore, more sensitive to any destructive influences that reach the coating.

From 28 to 30 pounds of red lead to a gallon of oil are necessary to make a good red-lead paint, for even when well ground it is liable to streak, curdle, or run, and is difficult for the painters to spread. The bulk of the red lead is so small compared with an equal weight of any other pigment per unit of covered surface, that the atoms of the red lead are well housed in the oil and better protected. Hence, when the conditions are favorable for a red-lead coating, it proves to be a more durable one than coatings made from other pigments that carry (as many of them do) in their composition the elements for their dissolution.

Fig. 10 illustrates the character of red-lead coatings when not well worked or brushed out in spreading. The porous character would disappear when spread on any surface other than glass.

The United States and other Governments have favored in the past a mixture of two or three parts of red lead and one of zinc oxide for the protective covering for lighthouses and seacoast iron structures. These coatings are harder than red lead alone, and better resist the action of salt-water spray, fog, and the abrasion from the sand-blast usual in such locations. But the result of some thirty years' experience with these mixtures has led to their abandonment for the reason that the oxide of zinc in the coating changed to a carbonate of zinc, and by its increase of volume disrupted the dried coating, exposed the ironwork, and the increase in the corrosion was markedly greater than with red lead alone, or red lead and silica, or red lead and graphite coatings.

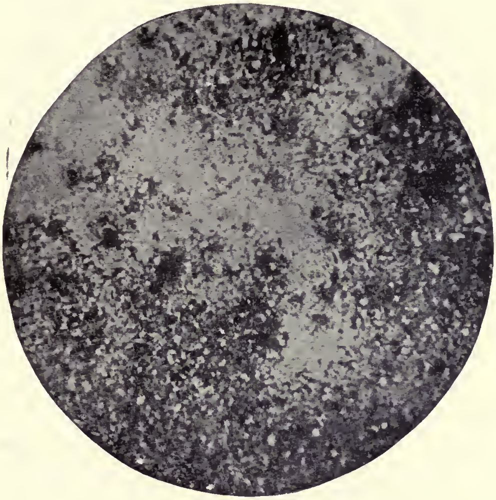

Fig. 10.—Photomicrograph × 100 of red lead and oil taken from a paint-pot and dried on a slide. The film is filled with air-bubbles and the coat is transparent in spots, although to the eye it looks solid. (M. Toch.)

Red-lead coatings soften metallic tin, hence for tin roofs they have not proven so durable as iron-oxide or graphite coatings, and are too expensive for that purpose. The effect of the red lead for such purposes is to form a white oxide of tin by the galvanic action between the two metals. The oxide of tin is free, and having no vehicle incorporated with it, is easily washed out by storms, leaving the iron plate entirely unprotected.

Fig. 11 illustrates the action of a red-lead-compound paint showing the character of that class of coatings for the protecting of surfaces, especially a ferric one.

Red-lead compositions are extensively advertised to keep indefinitely without setting, and that are ready for use at any time without further mixing or preparation. In all such mixtures, the red lead, or the oil, or both, are adulterated and will be found to be comparatively short-lived and unreliable whatever may be the guarantee, which in general lays more stress upon the extraordinary large surface that can be covered than the permanent character of the coating. As well expect a hydraulic cement ready mixed to be a suitable article for engineering use as an "always-ready" red-lead paint.

Fig. 11.—Photomicrograph × 100 of a film of dried paint taken from an iron pillar showing rust blisters. The dark spot is red lead and a fissure runs through the centre. The zinc oxide and white lead are white and are intact. (M. Toch.)

The setting or solidification of a pure or nominally pure red-lead paint is a characteristic chemical union between the oil and the lead, and without this action the paint is worthless. This chemical action is sought to be simulated in all compound paints by the liberal use of driers either incorporated in the vehicle by heat or by being introduced through the bung-hole of the barrel. The setting must take place eventually, and the better paint will be the one in which it is definitely provided for, and not left to the haphazard operations around the bung-hole.

One gill of crude mineral oil or heavy refined petroleum added to a gallon of red-lead paint will delay the setting of it indefinitely. It will dry superficially, as the oxidizing power of the red lead will ensure that essential, but the petroleum will always remain viscid in the coating and eventually destroy it by peeling soon after an exposure to a strong sunlight or heat, following or followed by a lower damp temperature or a storm.

Red lead, either in the form of a pigment or paste, when quoted as being "second quality," can be regarded not only with suspicion, but with a certainty that it is greatly adulterated or poorly oxidized from impure lead, or not properly washed or pulverized.

First-class manufacturers of red lead have no second-quality product that they are willing to have bear their brand or seal. There are a large number of red-lead corroders in the United States, and to the author's knowledge only one of the number advertises a second-class product. It may also be of interest to note that the United States Bureau of Construction, in its orders for red lead, specifies the make of one corroder as the standard of quality to which all tenders must conform.

A good red lead as it comes from the manufacturer is finely pulverized, as this point in a great measure governs the setting and running (creep, crawl, or curdling the painters call it). The atoms should be opaque, which indicates a good covering or light dispersing power. If the atoms are crystalline and more or less translucent, the paint will have a tendency to "tack." This effect does not always indicate that the pigment is deficient in other respects to form a durable coating; for the "tack" is sometimes due to the quality of the oil, and that the red-lead manufacturer has seldom anything to do with.

The adulteration of red lead and litharge can be readily ascertained by digesting a sample in a warm solution of nitric acid; the adulterants will remain undissolved.

Boiling hydrochloric acid will extract the iron oxide from the residue. If adulterated red lead is ignited there remains a mixture of yellow lead oxide and the red or other colored substances that have been added to the red lead.

Red lead boiled in hydrochloric acid is slowly converted into the chloride of lead with an evolution of chlorine gas. Dilute nitric acid only slowly dissolves red lead, leaving a brown powder.

Salt creates a chemical action on red lead that is liable to blister the coating and reduce the red lead to a metallic state.

Grimshaw recommends a mixture of red lead with painters' sizing to cover pine knots or yellow pine woodwork, instead of the usual shellac varnish. It forms a heavier coating than shellac, is equally or more resistant to the pitch, and is less liable to blister.

A gallon of pure linseed-oil will require not less than 20 pounds as a minimum quantity of pure red lead to 30 pounds as a maximum quantity for a reliable red-lead paint which will cover from 750 to 1200 square feet of metallic surface. These quantities of material at once remove red-lead paint from any comparison of cost with the oxide-of-iron and many mixed paints—principally in the form of proprietary goods, the ingredients of which are only known to the makers, and the character and performance of which will vary in quite as erratic a manner as the price paid for them.

The protective qualities of a well-oxidized pure red-lead and a pure oil paint, properly applied to any structure under any exposure, except to the action of hydric-sulphide gas, cannot be gainsaid. But what effect other than failure of it can be expected when a government engineer in charge of an important hydraulic construction, after cleaning the metal part of the work by the sand-blast, coated it with the following paint? "Red lead, 40 pounds, mixed with *three pints* of water to one gallon of raw linseed-oil for the first coat, and for the second coating, red lead, 40 pounds, three pints of water, three ounces of lampblack mixed with enough turpentine to make a paste, and one gallon of raw linseed-oil. It was found necessary to first moisten the red lead with water to prevent the paint from streaking and sagging. Without the water, a large proportion of turpentine and drier would have been necessary, *and this was considered injurious to the life of the paint.* In warm weather a slightly less quantity of red lead could be used" (or more water?).

Many kindred examples of such "how not to protect" structures can be cited, none, however, more conspicuous than the above when the engineer in charge and the character of the work are considered.

The substitution of water for turpentine in the amount here noted in order to *prolong* the life of the paint will be welcome news to the many manufacturers of that class of patent or proprietary paints who have heretofore deemed an addition of 20 to 25 per cent of water to the 7 to 8 per cent present in their green linseed-oil as about the limit of a whipped-in-oil vehicle. They can now proceed to water their stock of paint to a point where even the water in the financial part of their enterprise will seem in comparison but an insignificant pool. (The effects of watered oil is further considered in Chapter XXV.)

Litharge, PbO (Protoxide of lead). *Specific gravity,* 8.50 *to* 9.00.

Litharge as the first product in the oxidation of metallic lead to form red lead has been described. Another source of litharge is from the scum of melted lead or that from the smelting of silver-bearing ores. It is formed as an oxide by exposing to the roasting heat of a furnace the slag, or "matte," that on cooling forms into white or flake litharge. The part that hardens last is called "Massicot" or "levigated" litharge, and is ground in water, dried, and made ready for the market. It is a yellowish-red substance or an amorphous powder, and crystallizes in fine six-sided scales or plates. It is a yellow or reddish protoxide of lead, partially fused and semi-transparent. The yellow is the fused or hard pieces that require to be ground and levigated; the red atoms are the flakes. The difference in the color arises from the mechanical condition resulting from the manner and difference in cooling the roasted product, a rapid cooling giving a yellowish color, a slow cooling a reddish one.

By analysis it consists of the protoxide of lead, (PbO),

94.68% to 96.20% = 89.28% to 87.86% of metallic lead.
6.93% " 6.82% of oxygen.
2.89% " traces " the oxides of iron, zinc, copper, antimony, bismuth, etc.
4.36% " traces " arsenious, silicic, and carbonic acids.
0.49% " traces " lime.

The special furnaces employed and the manipulations of the charge during the heating and cooling processes applicable to the manufacture of red lead are requisite for a reliable litharge; also the same care in grinding and the subsequent operations to prepare it for a pigment or for other uses. Its integrity when used in a paint is affected by the same causes that affect a red-lead coating. It is adulterated, if possible, in a more barefaced manner than any red lead.

Orange mineral is made from the litharge "Massicot," also from white lead. In many cases refuse white lead is used as the base material. The material is placed in a reverberatory furnace and exposed to a moderate heat and a current of air and stirring as usual for producing red lead.

The carbonic acid in the white lead is expelled, leaving a protoxide of lead which absorbs more oxygen and produces a red lead of a lighter color than that made from litharge by reason that the oxidation is more complete.

Paris red is prepared by roasting the carbonate of lead to a litharge, the difference between the Orange mineral and Paris-red pigments being that the latter retains a little carbonic acid in its composition due to the different degree of heat employed in the furnace and the manner of cooling the product. Vermilionette is an orange-red pigment formed from the oxide of lead.

CHAPTER V.

WHITE LEAD.

White Lead, $PbCO_3$ (Hydrated Carbonate of Lead). Specific gravity, 6.465 to 6.480.

THE native anhydrous meta-carbonate of lead, ($PbCO_3$), called white-lead ore or cerussite, when pure is found in colorless crystals of the trimetric system. It is found in commercial quantities in all parts of the world where mineral lead ores are mined for smelting purposes. Pliny mentions the use of a native ceruse found on the lands of Theodotus at Smyrna.

The proto-sulphide of lead, (PbS), is the blue-lead ore (Galena) and is the principal source for the supply of metallic lead. White lead and the red oxide of lead are next to the oxide of iron, ochre, umber, and sienna, the oldest-known pigments. Dioscorides (B.C. 400), Pliny, and Vetruvius all mention the production of white lead by exposing metallic lead to the vapor of vinegar, giving the product the name of "Cerusa" and "Cerosa." Bergman in 1775 localized it as a carbonate of lead instead of an acetate, as it had before been considered.

White lead was used by the Egyptians as a cosmetic long before its employment for a pigment.

The mining and smelting of lead ore to produce metallic lead were practised by the Chinese 2000 years B.C. In the smelting of lead ore large quantities of the lead are oxidized to the red-lead "minium," the use of which as a pigment antedates the knowledge of producing white lead by corrosion. Moses commanded the Israelites to purify lead (called opheret) by fire.

The principal amount of white lead is produced by the so-called "Old Dutch Process." This process did not originate in Holland, where the recorded establishment of it does not appear before the sixteenth century. It was probably introduced into Holland by the Saracens. Venetian lead was early known for its purity and commanded a higher price than the Dutch-manufactured lead on this account. The establishment of the white-lead industry in England was almost synonymous with that of Holland, and evidently was introduced by Hollanders, hence the name "Dutch Process Lead." In this process thin perforated sheets of lead are exposed in gallipots containing a weak solution of acetic acid (water with 2½ parts of strong acid) or common cider vinegar. The pots are placed in long tiers, each tier being loosely covered with boards and stacked in large numbers, 9000 to 10,000 pots containing 60 or more tons of metallic lead. The bed of pots is then embedded in tan-bark, sawdust, stable litter, etc., that ferments and soon raises the temperature of the mass to 140° or 165° F. A quantity of vinegar containing 50 pounds of strong acid converts 2 to 2½ tons of lead into the carbonate of lead in about 100 days. The only attention the bed requires during the process of corrosion is to control the temperature of the mass by regulating the admission of the air to the interior of the beds by opening or closing the apertures left for that purpose. The corrosion is practically completed at the end of 60 days, but the lead is of light specific gravity, so it is the practice to allow the beds to remain unbroken for 30 or 40 days more, in which time the lead acquires a proper density. If the lead is allowed to remain in the beds too long, say 5 or 6 months, it is liable to become crystalline and transparent and will be of poor covering power. Care is necessary in the use of stable litter or that from flesh-eating animals, as they are liable to change the white carbonate of lead as it forms into a dark sulphide of lead from the sulphurous hydrogen evolved in the decomposition of the manure.

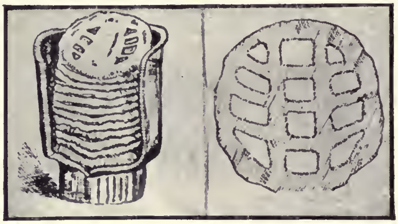

FIG. 12.—Sheet-lead buckles and pot.

At the time of stacking the air in the bed contains about 20 parts of oxygen; after 2 weeks it will contain only 17 parts; in 5 to 6 weeks, 7 to 15 per cent, while the carbonic-acid element will have increased from $\frac{5}{8}$ of 1 per cent to 23 or 27 per cent during the process of corrosion. From 30 to 40 per cent of the lead remains unchanged, which is separated from the carbonate by passing the contents of the pots through a series of rolls, beaters, and screens. The corroded lead is then mixed with water and ground between buhr-stones to an impalpable powder. Generally this part of the process is omitted by the quick-process lead manufacturers, because of the fine state of division to which it is necessary to reduce the metallic lead for these processes. The uncorroded particles are so intimately associated with the carbonate that they are indifferently eliminated in the separator, and if run through the water-stones, will cover the face of the stones with a coating of metallic lead that soon impairs their grinding power and imparts a dark color to the product.

If the preliminary washing before grinding is not thoroughly done to free it from the acetic acid (which is a drier) the powdered carbonate will dry in grains and lumps, and it may contain partly corroded or pure-lead particles, in which case the corrosion of them will proceed in the paint coating from the carbonic acid in the atmosphere. Added adulterants of any nature cannot prevent this secondary corrosion.

Silver in the metallic lead produces a pinkish cast in the corroded lead, while bismuth inclines it to a dark or gray color. Antimony, arsenic, iron, zinc, and other metals also have a great effect on the color of the corroded lead.

After grinding, the mixed carbonate and water is mechanically floated to remove any coarse particles, then pumped into large settling-tanks, where it is double-washed with pure soft water and bicarbonate of soda in solution to neutralize any trace of the acetic acid that may be present. After giving the lead time to settle in these tanks, the water is drawn off, and the pulp lead, carrying about 24 per cent by weight of water, is pumped to large shallow copper drying-pans and the water evaporated. This drying process requires from 6 to 8 days, the temperature of the drying-rooms being kept at from 140° to 160° F. The lead product when it leaves the drying-pans is pulverized and marketed as dry white lead or ground in buhr-stones with linseed-oil for a paste or mixed paint.

A modification of the Dutch Process Lead, known as "Pulp Process Lead," consists of taking the pulp lead from the settling-tanks and placing it in a tank of linseed-oil and subjecting the mixture to a high-speed mechanical stirring for a number of hours. Some of the water in the pulp lead is expelled, and rises to the top of the mixture and is drawn off; but a great part of the 24 per cent of water in the pulp is mechanically whipped into an emulsion or forced combination with the lead. Pulp lead is decidedly inferior; even if subsequently ground it does not bring it up to the standard grade of a white-lead product. Pulp leads are inclined to chalk more than the same lead submitted to the full process of drying, chasing, and grinding. They are more uncertain in taking tints, and, when applied in frosty weather or on exposed situations, are prone to peel. They also require more driers to aid in driving off the surplus water. Their low price is all that gives them a market.

By the "Old Dutch Process" the lead is neither oxidized nor carbonated at the expense of the acetic acid. The oxygen is derived from the air, and the carbonic acid from the tan-bark or other fermenting source. The vapor from the acid element as it is evaporated by the heat of fermentation merely serves to dissolve the oxide of lead as it forms, converting it into a basic acetate, which is again decomposed by the carbonic acid, the acetate being thereby set free to act upon another portion of the lead.

This is shown to be the mode of action by a modern process of corrosion, in which the protoxide of lead (PbO) is moistened with water containing about 1 per cent of the neutral acetate of lead (sugar of lead, $PbO.C_4H_6O_3$) and a current of carbonic-acid gas passed over it, the litharge being quickly converted into an excellent white lead.

There are many modifications of the "Old Dutch Process" that are referred to hereafter; all intended to improve the product, shorten the period of corrosion, and avoid the deleterious effect of the gases evolved from the corroding lead, upon the workmen. In fact, all the operations connected with the manufacture and use of lead products by any process, from the lead ore to a pigment, are exceedingly detrimental to the health of all persons so engaged, even with the best-known precautions.

When honestly and thoroughly done through the long chain of operations called the "Old Dutch Process," the product is as fine, smooth, and homogeneous in character as any known pigment, and can be used with little or no waste. It is particularly free from sulphur compounds, which invariably change lead from a carbonate to a sulphide, to the detriment of the color and life of the paint.

Even with the best of care in the corrosion, "Old Dutch Process" lead differs greatly in character. The product from the centre of the stack may differ from that at the side walls, where more moisture is present. An excess of moisture gives the grains a sugary appearance. The evenness of temperature in the stack, due to many causes, also the time of the year that the corrosion is effected, governs the quantity and quality of the product.

Commercial white lead is often inadequately corroded, washed, and ground. Pieces of uncorroded lead, tan-bark, and other substances from the ferment-packing, are incorporated in the pigment, subsequent decomposition of which in the mixed paste or paint discolors it and shortens the life of the paint. To such an extent is the careless corrosion of lead practised, that the brand of "Old Dutch Process" is called in derision "the happy-go-lucky process" by the advocates of the so-called "quick process." It is no longer a criterion of perfection in manufacture and purity, unless obtained directly from reputable manufacturers or dealers. Nevertheless, white-lead paste has held its former excellence and in some cases has been improved. It is also safe to say that but few corroders continued to use the Old Dutch Process, however desirable it may be to have the reputation for so doing, owing to the confidence that painters and users of paints have in its merits, which have been known and established for centuries.

Some of the modern processes of corrosion consist in the reduction of metallic lead into ribbons or wires, or subjecting the molten lead to the action of an air or steam blast, by which it is riven into small particles, greatly increasing the surface exposed to the action of the acetic acid, thus expediting the formation of the acetate of lead, which is afterwards corroded by passing carbonic-acid gas over it; the latter being generated in special apparatus, or by the hot products of combustion from gaseous fuel. These processes, while they cheapen and hasten the corrosion, have not improved the quality of the product or lessened the dangers to the employés.

The product by these latter-day processes is not only coarser in composition, but in some cases is decidedly crystalline, and carries the water of crystallization, that is afterwards set free in the grinding process, into the paste or paint, to their detriment, and the surface they cover, whether it is of wood or metal.

All gaseous fuel, unless purified by special processes, and with great care, as in the practice of purification of illuminating coal-gas, contains sulphurous-acid vapor in its composition. However little of this substance is taken up by the lead exposed to its action, its detrimental effects will be seen sooner or later in the product.

The sulphite of lead ($PbSO_3$), prepared by passing sulphurous oxide into a solution of neutral plumbic acetate (sugar of lead), is a white insoluble, anhydrous powder called "precipitated white lead." It is of comparatively recent use and is favorably reported upon for a pigment.

The hydrated carbonates of lead, formed by the direct action of carbonic acid on the hydrate of lead ($Pb.(OH)_2$), differs from the precipitated carbonates in being amorphous and perfectly opaque; whereas the precipitated carbonate is an aggregate of minute transparent crystalline grains. Hence the former are the best pigments; their greater opacity gives what the painters call "body."

In the German, Austrian, or Chamber processes of corrosion, the lead is used in sheets 1″×8″×12″, 1800 or 2000 sheets in a box, 8 boxes to a chamber that may contain 12 to 24 tons of lead. The walls of the chamber are lined with metal and heated by steam. The carbonic-acid gas is made by the fermentation of vinegar, yeast, and other substances, ammonia, phosphate of magnesia, etc., being added to hasten the fermentation. Carbonic acid from burning charcoal and other methods are employed for generating the carbonic-acid gas in great volume, for a quick corroding vapor to fill the chamber.

The Kremser white or Klangenfurt, a German corrosion process, uses the vinegar from dried grapes as an excitant to corrosion. The best quality of this process lead is claimed to be whiter than the "Old Dutch Process" leads and to cover equally as well.

Krem's or Crem's white is a poorer quality of the "Kremser process" lead.

Kremnitz white is a product from Kremnitz's (German) dry precipitation process.

Flake-white is a pure white lead in a scaly form rather than as crystals or grains—the usual form from the Dutch process. It lacks opacity or covering power.

The Clichy or French process is the principal quick-corrosion process used in France. The product is known as *Ceruse de Clichy.* It is entirely different from the other decomposition or precipitation processes mentioned before. The white lead is formed by passing carbonic-acid gas for 12 to 14 hours through a sugar-of-lead or litharge and acetic-acid solution, forming a subacetate of lead. The sediment formed is more or less crystalline, loose or coarse in grain. It takes up less oil than the Old Dutch Process leads, allows more light to pass through it, hence does not cover nearly so well.

Greneberg's (German) process consists of the action of carbonic acid on finely divided lead and litharge while being rolled constantly in tight metallic cylinders. The mechanical friction aids the corrosion at the expense of the purity and durability of the product, though there is less exposure of the workman to the corrosion fumes in this part of the process.

Milner's (English) process produces white lead in two days by the action of carbonic acid on oxychloride of lead (litharge) by grinding them together with common salt in water.

Pattison's (English) lead is a wet precipitation product—the oxychloride of lead, made by the action of muriatic acid on galena (lead ore).

The Carter (American) process is a modification or an improvement on the Kremnitz (German) process. Metallic lead is melted, and while molten is riven into fine particles, like flour, by a jet of high-pressure superheated steam. This amorphous powder, of a steel-gray or dark-blue color, is charged into a revolving cylinder 5 to 7 feet in diameter by 8 to 12 feet long. One end of the cylinder is connected to an exhaust-fan and the other end to a flue leading from a furnace where carbonic-acid gas is generated from burning charcoal. Generally the products of combustion from a coke fire under the steam-boiler of the plant are used for the corroding gas, the furnace gases having been washed and purified to free them from any sulphur present. The temperature of the revolving cylinder and the charge of powdered lead is kept at about 140° F. during the process. Dilute acetic acid and hot water are sprayed into the chamber at different times during the corrosion process, the stage of which is always accessible for inspection by removing samples of the lead without interrupting the chemical action of corrosion. The agitation or turning-over of the lead and its exposure to the heat is constant during the process. About 95 per cent of the lead is changed to white lead by this process instead of 60 to 70 per cent by the Old Dutch Process. The presence of antimony, bismuth, silver, zinc, and other metals, affects the color and quality of the lead by this process as well as in all others. The treatment of the white-lead powder after it leaves the cylinder to form the dry white lead or the paint paste is similar to the Old Dutch or other processes. The powder is repeatedly washed with water to free it from the acetic acid, ground in water to a pulp form, and floated through a number of tanks and allowed to settle. The greater the care used to eliminate the acid the more reliable will be the product.

The products of all of the above processes, as well as of many other quick processes, vary in some degree of quality or form of the white-lead atoms from that of the "Old Dutch Process." The latter can be said to rank as the standard for purity, fineness, and all other qualities which are indifferently imitated in most of the quick-process products, the Carter being probably the best of them.

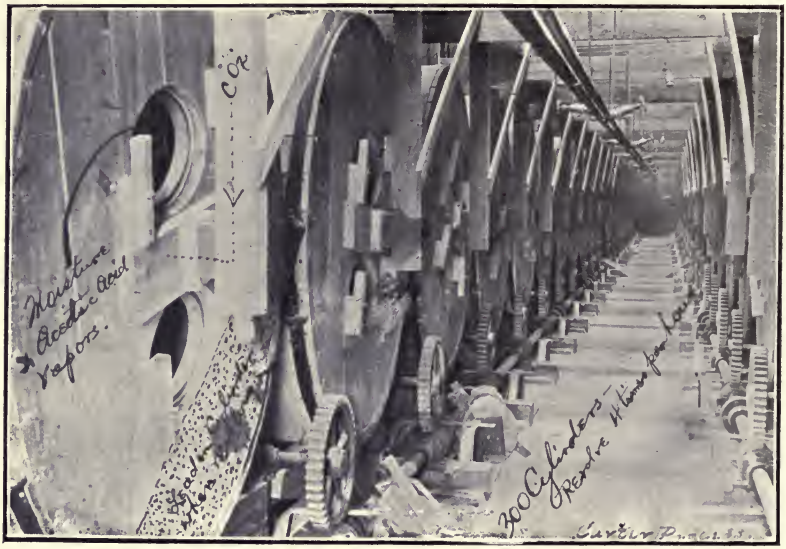

Fig. 13.—The Carter process for manufacturing white lead.

Many of the quick-process leads contain acetic and carbonic acids; the former, being added in excess of the amount necessary for a natural rate of corrosion by the old methods, remains in the corroded product and requires a more thorough washing to remove it than it customarily receives. The acid element is often strong enough to redden litmus-paper, which would be discovered if the dry white-lead powder could be obtained to make the test. The acid causes loss of opacity and rapid chalking. The corrosion of the lead is simply removed from the corroding stack to the paint coating, the carbonic acid and the moisture required in this secondary process are both present in the atmosphere, and not only the carbonate of lead is formed, but this is further reduced to a subcarbonate of lead; the latter change constitutes the chalking stage in the decay of the coating. Acetic acid and uncorroded lead, left by imperfect washing and grinding, are frequently present in commercial white leads. Ten per cent of lead acetate is often found in the "flake-whites." Most of the quick-process or impure leads come to the market in some form of "whites" with a misleading trade-mark.

The report of the Committee of Experts appointed by the English Home Secretary to investigate the manufacture of lead products, as to the character and quality of the product, also their effect upon the health of the workmen, was: That they visited forty-six establishments using various processes for manufacturing white-lead pigments, all of which were dangerous to the health of persons so employed, and while some of the substitute leads were cheaper to make, and possibly a little less injurious to the workmen, their products were far from equalling in quality those from the "Old Dutch Process," and they could not recommend either the processes or products as against the "Old Dutch Process" leads.

Baryta white is prepared from the native sulphate of barium, or from the carbonate of baryta, artificially treated with sulphuric acid. (See Barytes, Inert Pigments, Chapter XVIII.)

Krem's, Nottingham, and Newcastle whites are pure white leads differing only in the process by which they are made. Hamburg, Holland, and many foreign-made whites contain from 3 to 60 per cent of barytes and chalk, and are adulterated compounds of white lead. Venice white generally consists of equal parts of white lead and barytes. All pastes and mixed paints classified and marketed as "whites" are usually only adulterations of white lead, and no responsible and honest corroders of white lead ever so denominate their products. The name "white," whatever its trade prefix, should usually be viewed with suspicion of its quality. (See tests of white lead on the following pages.)

About 110,000 tons of metallic lead are annually corroded to white lead, in the United States, by the various processes, or about one-third of the total production of the metal product.

There are twenty-two manufacturers using the "Old Dutch Process" in the United States, and five using the "Quick Process."

The first white lead corroded in the United States was by Samuel Wetherell in 1810 at Philadelphia, followed by Christian Bielen in

1811 at Pittsburg. Cincinnati also had a white-lead plant shortly afterward.

*Electrolytic White Lead.**

This process is a radical departure from all of the other processes for producing white lead, in not employing acetic acid, but by acting upon the lead in the form of pigs with nitric acid, which is generated by electricity. The process consists of four consecutive steps:

First. The electrical preparation of nitric acid and sodium hydroxide.

Second. The action of the nitric acid on the metallic lead forming lead nitrate, $Pb(NO_2)_2+H_2$.

Third. The reaction of lead nitrate and sodium hydrate to form lead hydroxide, viz.: $Pb(NO_2)_2+2NaOH=Pb(OH)_2+2NaNO_3$.

Fourth. The combination of the lead hydroxide and sodium bicarbonate to form lead carbonate, $Pb(OH)_2+HNaCO_3+NaOH+H_2O$.

Reactions 2 and 3 may not take place strictly as given, which are the theoretical combinations, but some approximate reactions are had, for the extra hydrogen present is liberated at the electrode.

The chemical operations in the process are briefly:

First, a solution of nitrate of sodium ($NaNO_3$) is decomposed by an electric current from a dynamo, the strength of the solution not being important—10° Baumé or one pound per gallon suffices. This solution is put in a series of wooden cells divided into two compartments by porous partitions. At the positive electrode is fastened a pig of lead, at the negative a sheet of copper. On applying the current the nitrate of sodium is decomposed according to the equation 1 given, nitric acid collecting at the positive electrode and sodium hydroxide at the negative. The nitric acid at once attacks the lead and forms lead nitrate, which dissolves (equation 2) the hydrate of sodium, producing no effect upon the copper at the negative pole.

Finally, both solutions are separately drawn off and mixed, as desired, in quantitative proportions in any suitable vessel. The result, as shown in equation 3, gives the lead hydroxide as a white amorphous precipitate and leaves the nitrate of sodium in solution.

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* "Electrolytic process for the manufacture of white lead." A paper read before the American Chemical Society by E. P. Williams. Reprinted in *Electrical World*, Sept. 14, 1895, pp. 289-90. Mr. Arthur G. Brown, Inventor, 1892.

This is practically the original nitrate, and can be used over and over again as the source for more nitric acid. The loss of the sodium is small, and a little additional fresh sodium hydrate restores its strength.

The lead-hydrate precipitate ($Pb(OH)_2$) is then filtered from the sodium hydrate by a rotary separator, and the nitrate of sodium returned to the original reservoir.

The fourth step is in some respects the most interesting of all, and consists in adding to the lead hydroxide a solution of bicarbonate of soda (or the normal carbonate). Reaction 4 at once takes place. It will be noticed that the sodium hydroxide is the product in solution, and lead carbonate the precipitate.

The sodium hydroxide removes most of the impurities, if there are any, in the hydrate of lead. It dissolves any salts of alumina or zinc present, and it removes the organic matter. These impurities appear in the solution, leaving the precipitated lead remarkably fine and white. The hydroxide of sodium is again converted into bicarbonate by passing carbonic acid into it, and this is used again. Thus the main agents in each of the two principal steps, the nitrate of sodium and the bicarbonate of sodium, are made to do duty over and over again with but slight additions to restore the strength.

The use of free nitric acid in the process is objectionable, as under the influence of electricity it breaks up with intolerable fumes; also for other reasons. Acetic acid is also objectionable for the same reasons, hence the recourse to sodium or potassium nitrates for the reactions.

The cost of white lead by this process is but a fraction of that by the "Old Dutch Process," as the lead is used as it comes from the smelting-furnace in pigs and requires no remelting or casting into buckles or shreds, as in the corrosion processes, and the whole process is complete in a day, or, for that matter, in an hour, as all of the reactions take place rapidly, if not instantaneously, no free acids are used, and the sodium compounds are recovered, as noted.

The texture of the lead product is almost molecular in fineness and does not require grinding, it being so fine that it remains suspended in the water for a long time, and in order to filter it a special brand of cloth is used, as filter-paper would scarcely retain it.

Its covering power applied side by side with the Dutch Process lead appears to be equal to it, possibly a little better, but never found to be less.

Whether the electrolytic lead will displace the "Old Dutch Process" lead to any great extent remains for time to determine. The French or Clichy process lead, or "Clichy white," was thought at first to be a revolutionary one, but the product finally proved to be decidedly inferior to the Dutch Process lead, from its crystalline character. It does not give the opacity or body, or spread as well under the brush, or cover as much surface as the Dutch Process lead.

The "Dutch Process" lead forms a globular atom, viz.: two atoms of the carbonate, $PbCO_3$, and one atom of the hydrate of lead, $Pb(OH)_2$, but this composition does not always appear to be of constant quality, as much depends upon the care given during the corrosion part of the process.

Lead hydrate, or the hydrate oxide, is a white amorphous substance. The carbonate may be either globular or crystalline, depending upon the methods of its preparation. Now, certain qualities of these two forms are quite unlike, and this explains why the use of one has continued and the other been abandoned as a pigment. The atoms of the one form are said to be from $\frac{1}{10000}$ to $\frac{4}{10000}$ inch in diameter, and in the grinding with the oil take it up somewhat as a sponge absorbs water. In the "Dutch Process" leads, when properly corroded, the atoms are globular, and to this is due the greater body and permanency of the paint over that from any of the quick-process leads. The crystalline form does not absorb near the same amount of oil, no matter how finely it may be ground, as the surface of the crystals, either whole, as formed, or crushed in the grinding, are impervious and do not have the same light-dispersing or reflecting power. Hence their poor covering quality; and they do not bond to or in the vehicle as well—they save oil.

If by the electrolytic process it is possible (as it is claimed) to produce a pure carbonate of lead, or a mixture of the carbonate and hydrate of lead in any proportion required, and the product proves to be fine and globular instead of coarse, granular, or crystalline, there should be no doubt regarding its merits, but the few hundred tons thus far spread do not afford sufficient data for a wholesale abandonment of the "Old Dutch Process" with its centuries of established reputation.

Mr. E. Bailey, York, England,* has invented a so-called electrical process for the manufacture of white lead and other metallic-oxide compounds. An electric arc keeps the lead in a molten state. The melted lead is then acted upon by gaseous vapors blown through it

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* *London Electrical Engineer*, Jan., 1901.

to produce the carbonate or oxide of lead. The fumes produced are blown into chambers having canvas or fine-fabric cloth covers or roofs. The fine powders fall down and are collected for pigments, and require no washing. The uncondensed vapors escape through the cloth screens to the atmosphere or stack. A saving of 50 per cent is claimed for the process over that of the "Old Dutch Process," but like all other quick-process leads, the merits of the product are yet to be established.

There never has been any difficulty in quickly corroding or oxidizing metallic lead or zinc for use as a pigment. The difficulty with all quick-process leads is in the quality of the product, and, though the processes are patented from Dan to Beersheba, the ornate devices and claims of the patent-office document do not put the wearing and other desirable qualities into the product that the patent claims allege to be there.

There is nothing electrolytic in the Bailey process. The melting of the lead by an electric current previous to or during the action of the corroding gases produces no electrolysis in the molten metal, the heating of which could be as readily and more cheaply done by a coal or other fire. The collection of the metallic vapors by screens is an old method of pigment manufacture—in use for the production of sublimated lead, as described in Chapter VI, and is void of electrolytic action.

CHAPTER VI.

WHAT CONSTITUTES A GOOD WHITE LEAD.

Mulder's and Phillips's analyses determined that there are three varieties of white lead in the best classes of that product experimented with under the general formula of the hydrated carbonate, $PbCO_3$, viz.:

$$2Pb''CO_3.\ Pb''H_2O_2;\ 5Pb''CO_3,3Pb''H_2O_2;\ 3Pb''CO_3.\ H_2O_2.$$

A properly corroded white lead should contain oxide of lead combined with water—water lead (hydrate of lead, $Pb(OH)_2$.), from 25 to 32 per cent, which in its effect upon the vehicle is similar to red lead; it absorbs oxygen and hardens the coating by converting a part of the oil into a soap that has no covering power whatever. The other 75 to 68 per cent should be oxide of lead combined with carbonic acid (carbonic-acid lead), that really injures the oil in the paint, but gives all of the covering properties that the paint possesses. The chalking of white-lead paint is due to this 75 per cent of carbonic-acid lead. A paint composed wholly of carbonic-acid lead will, in a short time, chalk as freely as a whitewash. The carbonic-acid lead gives the whiteness or color, the water lead, the hardness or durability to the coating.

In the following table from Heiss's experiments,

Number 1 is a good dense white lead. Specific gravity, 6.32
" 2 " dry white lead. " " 6.50
" 3 " crystalline transparent lead. " " 6.05

	Number 1.	Number 2.	Number 3.
Oxide of lead	85.95 per cent.	86.18 per cent.	83.53 per cent.
Carbonic acid	11.14 " "	10.44 " "	15.70 " "
Combined water	2.91 " "	3.38 " "	0.77 " "

Another comparative table is:

	Lead.	Carbonic Acid.	Combined Water.
White lead, best quality	86.80 per cent.	11.16 per cent.	2.00 per cent.
" " 2d "	86.24 " "	11.68 " "	1.81 " "
" " 3d "	86.03 " "	12.28 " "	1.68 " "
Residue lead	84.69 " "	14.10 " "	0.93 " "
Improperly corroded or useless lead	83.47 " "	16.15 " "	0.25 " "

In Prof. Hurst's analyses of four samples of "Old Dutch Process" white lead, the carbonate ranged from 65.35 to 72.15 per cent, the hydrate from 25.19 to 36.14 per cent, and the moisture 0.42 per cent to *nil.*

Mr. Converse's analyses of five samples of the best brands of American "Old Dutch Process" leads gave

Lead carbonate	85.32	79.37	78.58	77.98	69.96
" hydrate	14.83	19.80	20.11	20.60	30.19
" oxide	.....	.....	1.48	1.48	.....
Water	0.03	0.21	.....	.....	0.07

A very hard white lead that contains no water lead will not harden when spread, but brush off like a lime whitewash. When this occurs where the necessary amount of oil has been used, the painter can be quite sure that the lead is a poorly corroded or quick-process lead, or a synthetically formed lead from an acid-solution process. Carbonate of lime (chalk, whiting), gypsum, and other so-called inert substances added to such a lead do not correct this chalking; they only disguise it for the time being, and increase the tendency of such lead paints to turn yellow and lessen their covering power.

All white lead on external exposures is liable to chalk, because it contains too much carbonic-acid lead as it comes from the manufacturer, or has taken another portion of carbonic acid from the atmosphere at the expense of the water lead, and formed a subcarbonate of lead (the chalk product, $PbCO_2$), or has too little oil in it when spread, or has not been well ground in the oil. Paints thus affected, if brushed over with a coating of white lead *ground with an excess of oil,* will prove to be more durable and less affected by future chalking than the original coating, or a new heavy coat from the same lead.

The formation of a lead soap in the ordinary process of grinding and mixing white-lead pastes or paints is a disputed point by paint chemists. But the lead hydroxide and the free linoleic acid in linseed-oil, if acetic acid is present in the white lead, *will combine* and form a lead-soap mixture. The paint containing this soap, on exposure to the weather, soon loses its lustre and will crumble or chalk.

The presence of lead soap in many, if not the most, of white-lead paints is shown by Prof. Church, in his "Chemistry of Paints and Painting," as follows: "Upon a piece of glass place a small quantity of the white-lead paint, and add a 10 per cent solution of sulphuric acid. Work the mixture together with a glass rod or spatula into a cream-like condition. The acid will soon destroy the oily or hydrofuse character of the paint. With zinc white or baryta white in oil no such admixture is possible, for in these paints the oil will not saponify owing to the absence of an acid."

Mulder's and other experiments proved that the chalking of white lead was due solely to the absence of water lead in the pigment, unless the lead was badly adulterated, in which case this effect was directly traceable to the adulterant used.

In general, all the latter-day-process white leads are more inclined to chalk than the "Dutch Process" leads. This arises (as stated before) from the smaller amount of water lead in their composition, and being of a crystalline instead of a globular form. In the grinding process these crystals or grains are broken down, and the combined or formative water necessary for their existence in the form of crystals is dispersed, rendering the broken lead atoms more sensitive to the attack of the atmospheric carbonic-acid element, that finds in their sharp angular form a more favorable surface to act upon. Only a comparatively slight action of the carbonic acid on the freshly crushed atoms of the lead is required to change it to the subcarbonate, and leave it free to be brushed off by friction or washed out by storms.

Old white lead, or that which has been ground in oil to a paste for a year or more, chalks decidedly less than recently corroded lead, by whatever process it is made. The atoms of the pigment in the case of old lead have had time to release themselves from the tension due to their formation and grinding. Adulterations do not prevent these inexorable chemical changes in the lead pigment; they only increase the disintegrating action.

If oxide of zinc is used to give hardness in place of the water lead in paints exposed in open air, the atmospheric moisture and carbonic acid changes the oxide of zinc (ZnO) to a zinc carbonate ($ZnCO_3$) whose volume is nearly double that of the oxide from which it was formed in the hardened paint, and peeling takes place instead of chalking. The cheaper forms of zinc oxide contain zinc sulphite, which blackens the paint and otherwise injures the coating.

If gypsum, barytes, or silica are used for the adulteration, they lack both in covering and light-dispersing (coloring) power, and, from their sharp, angular, or irregular form as pigment-atoms, do not bond themselves in the oil, for which they have no affinity, nor enter into combination with, or bond to the covered surface. They prevent chalking only as their presence leaves less white lead to chalk, even if they do not actually increase its tendency towards that change, as the sharp, rough surface of the paint containing these adulterants holds the atmospheric moisture and gases closer and longer for their action. (See Decay of Paint and Inert Pigments, Chapter XXVII.)

White lead unites thoroughly with the oil. Zinc white combines, but very slowly; barytes does not combine at all. All pigments that contain crystals or are granular are deficient in the light-dispersing power, even if they have the spreading quality. The granular character of quick-process white lead is its great weakness.

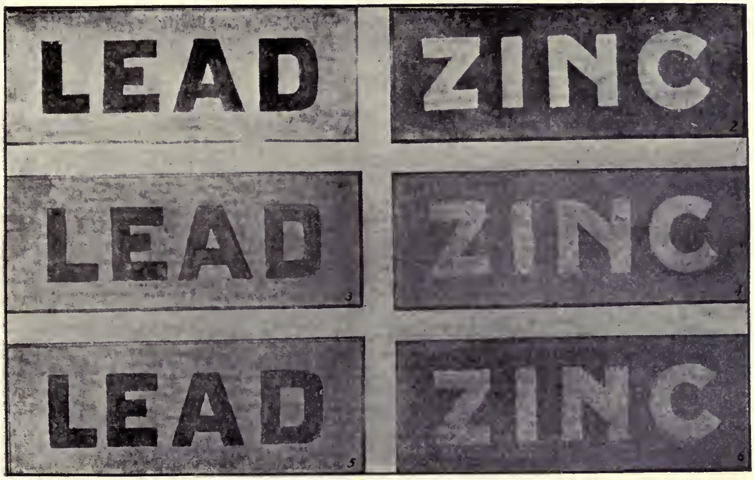

FIG. 14.—Effects of sulphurous gases on white lead.

Background in zinc white.
Lettering in white lead.

Background in white lead.
Lettering in zinc white.

The quality of the vehicle has much to do with chalking and the decay of white lead. A good linseed-oil will better preserve a poor, or an adulterated white lead, than a poor oil could the best of white lead.

Pure white lead is soluble in dilute nitric acid. A sample treated with this reagent should pass entirely into solution, leaving no residue. If the sample is in the form of a paste or paint the oil can be removed by washing it with benzine or ether, and the powder, when dried upon blotting-paper, should leave no stain.

The action of sulphuretted hydrogen upon white lead is that the sulphur element unites with the lead to form the sulphide of lead (PbS), which is a dark color. Further exposure changes the sulphide to a sulphate ($PbSO_3$), which is white and of good covering power. Hence the full change would not be detrimental to the coating in point of color were not these changes in the dried coating attended by a change in the volume of the lead-atoms at each step in their progress from a carbonate to a sulphate that ensures a forced disintegration of the coatings. (See Decay of Paint, Chapter XXVII.)

The cause of white-lead paint, when spread over darker colors, deteriorating after a short period and showing dark, is not alone owing to the changes mentioned above, but also that the fatty acids in the oil gradually expel the carbonic acid in the lead-atoms and form a clear lead soap, through which the darker colors beneath show.

Adulteration of White Lead.

The adulteration of white lead under the forms of a paste or mixed paint has reached a point where the multitudinous trademarks under which they are marketed are *positively* of no value to determine their quality; the only safety lies in purchasing from responsible business firms of national reputation for the standard quality of their products and business methods.

A late examination of commercial white-lead pastes purchased in the open market resulted as follows:

Seventy-five different white-lead pastes, under 29 different trademarks and symbols, embellished with 14 qualifying adjectives, and made by 17 different manufacturers, plus 1 unknown firm that furnished 14 different brands, were analyzed by 16 different analysts. The condensed results are, viz.:

Sixteen had no white lead in their composition, but were mixtures of barytes, silica, gypsum, zinc oxide, or whiting in some proportion of three or more of these substances.

Fifty-nine of the samples had white lead from 1.24 per cent to 47.62 per cent, and averaged for all 23.35 per cent of lead.

Seventy of the samples had barytes from 15.60 per cent to 86.37 per cent, and averaged for all 49.61 per cent. One or more of the above adulterants was used with white lead of uncertain quality for the balance of the paste.

In 5 of the samples silica replaced the barytes, otherwise the usual group was unbroken.

Seventy-five of the samples had oxide of zinc from 59.20 to 3.60 per cent, averaging for all 27.48 per cent. A free use of gypsum and whiting aided the white lead to give the paste a semblance of a pure white-lead product.

Thirty-two of the samples had sulphate of zinc in the paste from 84.85 to 0.88 per cent, averaging for all 22.09 per cent.

Five samples had chalk from 24.30 to 0.85 per cent, averaging for all 9.60 per cent.

Wherever carbonate or sulphate of lime was used it was at the expense of the white lead.

The adulteration of all of the brands, other than the 16 that had no white lead, ranged from 99 to 44 per cent, and averaged for the 59 pastes 80.4 per cent.

In 5 of the samples oxide of zinc was mentioned as constituting a small part of the paste, but nothing was said about the 30 to 40 per cent of barytes in their composition, or of a like amount of the other adulterants, or the *small amount* of white lead.

One sample had a notice that $1000 would be paid if the white lead in it was not pure. It had no white lead in it.

One sample offered $100, same conditions as above. It was of the same character. No white lead in it.

One sample had a $250 penalty for any imitation of the lead in it, or of the label on the package. It had 99 per cent of adulterants. Possibly a piece of the label might have fallen into the paste before analysis of it.

Probably the above adulteration record represents the larger number of commercial white-lead and tinted-color paints in the market. Unfortunately, most of them get juggled off, and generally at the price of really first-class paints; but so many people are willing to be humbugged to save a few cents on a pot of paint that it may be a mistake to enlighten them on the subject. What the character and quality of the oils are that form an essential part of all these adulterated and misleadingly named compounds, one can readily imagine. Surely they are equally deceptive and uneliable.

Maize-oil is used frequently to the amount of 25 per cent in the grinding of paint pastes and paints to prevent them from settling in the package. It is a non-siccative oil, and while not exerting any materially bad influence in a paint, its use with linseed-oil in any quantity can only be considered as an adulterant. Its cost is about one-half that of commercial linseed-oil. Its use requires more driers.

The use of 10 to 15 per cent of barytes in a white-lead paint may not be particularly objectionable in point of durability, if the lessened cost is the object desired. Lead pigments do not cover so well with barytes, but zinc oxide *covers better;* barytes gives weight that the zinc is deficient in. Some master painters advocate the use of barytes for the reason that it brightens dark colors and saves oil; but ignore the fact of its darkening light colors, also its tendency to yellow them from the sulphur element in its composition and its general deficiency in covering power. The advantages in any case do not warrant the use of from 50 to 80 per cent of this or any other substance which does not unite with the oil, and of themselves are unfit for a paint. As a rule, no responsible paint firms will offer such paints under their own names.

Zinc oxide is often mixed with white lead for other than adulteration purposes. It is added to correct the tendency of pure white lead to turn yellow from the action of sulphurous fumes in the atmosphere. It makes the paint harder, and possibly prevents "chalking" to some extent, as there is not so much lead to chalk, but adds a tendency to peel on outside exposures—a result worse than chalking. It is difficult to get a homogeneous blending of the two pigments so individually unlike in character, owing to their different processes of formation. Their mechanical association is far unlike that of a neutral whole, even with the best of supervising care in blending them.

Many of the difficulties in mixtures of white lead and zinc oxide are overcome by the use of a natural admixture of the lead and zinc in the form of a pigment known as sublimed lead or white paint, hereafter described.

White Lead vs. Zinc Paints.

Mr. G. R. Henderson, of the Norfolk and Western Railroad, reports a series of exposure tests to determine the efficiency of lead and zinc paints. For the different materials he reaches the following results:

"*Tin.* The best results were obtained with the first coat of white lead and second coat of white zinc. The second coating of zinc gave generally the best results, and the second coating of lead the worst.

"*Galvanized Iron.* The same remarks apply to galvanized iron that are given for tin.

"*Sheet Iron.* The mixture of one-third white zinc and two-thirds white lead, for both coats, gave the best results on this material, and in general the zinc paints gave better results than the lead paints.

"*Poplar.* The second coats of zinc showed up well on poplar, no matter whether the priming coats were white lead or white zinc or mixed lead and zinc. The lead second coating showed up the worst on this material, but in each case where the second coat was of zinc, totally or partially, the paint was in a perfect condition.

"*White Pine.* The remarks made relating to poplar apply to white pine also.

"*Yellow Pine.* This material seems to be difficult to properly treat with paints; the best results were obtained with the first coat of lead, and the second coat of lead and zinc mixed. Where the first coat was of lead and zinc mixed, or entirely of zinc, the results were poor throughout, which seems to indicate that as a general thing the lead is better for priming on this material.

"*Conclusion.* The lead priming and zinc coating is generally good for tin, galvanized iron, poplar, and white pine. Sheet iron showed up best with both coats of mixed paints. Yellow pine appeared best with the first coat of lead and the second coat of lead and zinc mixed. Comparing the materials which were painted, we find that generally poplar retains the paint better than white pine, and would, therefore, be preferred for siding on buildings, etc. Yellow pine seems to be the worst of all for this purpose. Black iron, as a whole, seems to retain the paint better than either tin or galvanized iron."

Tests for White Lead.

There are many tests for the purity of white lead, a simple one being to put a globule of the paste or dry powder in a cavity formed in a piece of charcoal, and expose it to the heat of a common blowpipe, readily extemporized in any shop. If even 10 per cent of adulterants are present it will not be possible to melt the mass.

White lead is tested for barytes by dilute nitric acid, in which barytes is insoluble, while the white lead passes completely into the solution. Whiting and chalk are detected by the nitrate solution yielding a white precipitate with oxalic or sulphuric acid or oxalate of ammonia, after having been treated with sulphuretted hydrogen or a hydrosulphuret to throw down the lead.

White lead dissolves with effervescence in hot hydrochloric acid as chloride of lead, which crystallizes into needles on cooling. Dilute nitric acid easily dissolves white lead with effervescence and an escape of carbonic-acid gas. White lead heated on a knife or piece of metal turns yellow. Sulphuretted-hydrogen fumes in the air turn white lead gray.

Substance.	Conduct towards		Heated before the Blowpipe.
	Muriatic Acid.	Caustic Soda.	
Whiting or chalk in any form.	Soluble with effervescence.	Unchanged.	Becomes incandescent and turns tumeric brown after cooling.
Commercial white leads. Pearl and other whites. Carbonate of lead, etc., quick-process leads.	Soluble with effervescence and deposition of small crystals.	Soluble without residue, or if of poor quality, 80 per cent will only be dissolved.	Coating formed on the charcoal is citron-yellow while hot, sulphur-yellow when cold; is easily fused with metallic beads.
Pattison's white lead. Lead oxychloride.	Same as above.	Same as above.	Same as above.
Zinc white or oxide.	Soluble, no effervescence.	Soluble without residue.	Yellow while hot, white when cold.
Antimony white. Antimonious-acid pigments.	Same as above.	Same as above.	White, easily volatilized, metallic globules which give off white smoke.
Bone-ash, Bone-black. Phosphate of calcium, $Ca_4(PO_4)_2$. (Basic steel furnace slag.)	Soluble after heating. Effervescent at first.	Unchanged.	Unchanged, but becomes incandescent.
Barytes, Blanc-Fixe, mineral white, and other pigments of the native sulphate of barium.	Unchanged.	Unchanged.	After ignition, if moistened with muriatic acid, gives off sulphuretted hydrogen vapor.
Gypsum (Hydrated sulphate of calcium).	Unchanged.	Unchanged.	Incandescent, like barytes. If heated in a tube, gives water vapors, etc.
China, pipe, potters', and other clays.	Unchanged.	Unchanged.	Incandescent, same as barytes and gypsum. If moistened with a solution of cobalt, and heated by the blowpipe, turns blue.

It is not generally known that dry white lead and oil combine with such energy that if linseed-oil is poured upon a large quantity of the lead, and the mass is allowed to stand a few hours, the temperature of the mass becomes so high that the oil is carbonized and colors the mass dark or even black. All white-lead paste is liable to turn brown if exposed freely to the air, hence should be kept closely covered, or water be kept on the paste when the package is opened.

Gmelin states "That the 'Old Dutch Process' white lead diffused through water, under the microscope appears as non-crystalline, round, and oval globules, .0001 and rarely .0003 or .0004 of an inch in diameter, while in the quick-process leads the globules are distinctively larger and more transparent and crystalline."

Dry white lead is tested by heating 100 grains red hot and stirring it for a moment. Its loss in weight by driving off the carbonic acid should be from 13 to 16 grains. If more or less loss is incurred, the lead is probably adulterated, and should be submitted to further test to determine the character of the adulterant, as shown in the table opposite.

Sublimed Lead, $PbSO_4$. Specific Gravity, 6.258.

Sublimed lead is a by-product obtained in the smelting of non-argentiferous lead ores. It is known in the trade as Joplin lead, from its place of manufacture, Joplin, Mo.; also as Picher lead, from the name of the manufacturing company. It is made in two colors—white, suitable for all purposes that the hydrated carbonate of lead is used for; and blue, which is a preferable color when used as a paint for iron. Both colors are used in the manufacture of india-rubber articles. The chemical composition of sublimed lead is sulphate and anhydrous oxide of lead, both amorphous; the good qualities of the white are also present in the blue-colored product. There is a small percentage of zinc in the Missouri lead ores, which in the process of smelting is converted into zinc oxide and is found in the sublimed-lead product, as may be seen in the analyses of a sample of the white product given on page 84.

The blue pigment owes its color to the lead sulphide and carbonaceous matter from the bituminous coal used as a fuel in the smelting-furnace.

Sublimed lead is prepared in special furnaces, the process being patented and known as the "Lewis and Bartlett Bag Process for collecting lead fumes." The process has been mentioned and described in more or less detail in the following papers.

Analyses Substances.	Averages.	Substances, Per Cent.	
Sublimed lead, $PbSO_4$	65.46 to 65.00 per cent.	Metallic lead,	71.831
Protoxide of lead, PbO	25.85 " 25.89 " "		
" " zinc, ZnO	5.95 " 6.02 " "	Metallic zinc,	4.808
" " iron, Fe_2O_3	0.03 " 0.03 " "	Oxygen combined,	20.508
Calcium oxide, CaO	0.02 " 0.02 " "		
Carbonic acid, CO_2	1.53 " 2.00 " "	Carbonic acid,	1.765
Sulphuric acid, SO_4	0.04 " 0.00 " "	Iron, lime, and insoluble matter,	0.130
Insoluble matter	0.08 " 0.08 " "		
Water	0.85 " 0.69 " "	Sulphur, water, and loss,	0.958
Loss	0.19 " 0.27 " "		
			100.00

Mineral Resources of the United States, 1883–4, p. 427; *Engineering,* 1884, p. 495; *Engineering and Mining Journal,* Vol. XL, 1885, p. 4; *B. und H. Zeitung,* Vol. XLVII, p. 346 (describes the works of the Bristol Sublimed Lead Company, Bristol, England, where the process is in operation); *Prerass Zeitsch,* Vol. XVIII, p. 195; *Fresenius Zeitsch,* Vol. VIII, p. 148; *Transactions of the American Institute of Mining Engineers* (Washington meeting, February, 1890), illustrated.

The galena ore is first smelted with coal and slaked lime in the special furnace, using an air-blast to obtain the required heat, about 800° F.; the hotter the fire the more lead is volatilized, and the more "fume" is produced.

The *philosophy* of the process is that galena ore, or the native lead sulphide, when heated to nearly a white heat, vaporizes slowly, and the vapors in contact with an excess of air passing through the furnace burn into lead sulphate. Simply heating a mass of galena ore does not, however, form the sublimed-lead product. When the ore is properly roasted in the special furnace the temperature required to effect the change to sublimed lead is far below that required in the vaporization of lead sulphide. The ore when rapidly heated, even if it does not actually vaporize, has a tendency to do so, which is sufficient for the sublimation process, and under favorable conditions will burn at a dull-red heat.

The process is the same in principle as that used in the collection of the oxide of zinc. The use of "fume" from the smelting of lead for a pigment is very old. Bishop Watkins, in his scientific works in 1778, mentions the use of *gray fume* for a paint; but its color was then objectionable as against the white product of corroded white lead by the "Old Dutch Process."

The direct fume-product from the combustion of galena ore is not yet sublimed white lead. The products of the smelting-furnace are pig lead, pasty slags containing more or less lead, zinc, and other metallic constituents of the galena ore and "fume." The latter is drawn off by an exhaust-fan through a settling-chamber to a bag-house which contains a large number of woollen bags for filtering the fume out of the combustion gases. This "fume" is a lead-colored, impalpable powder known as "blue powder." It is ignited and allowed to burn for several hours, which converts it into white coherent crusts. These crusts, with some oxidized ores, settling in the flues and hearth slags, are next charged into a special furnace and exposed to a very hot coke fire. The products of this smelting are pig lead, slags poor in lead as waste material, and the "fume," which is now a perfectly white impalpable pigment suspended in the air. This is drawn through a series of cooling flues, where a further purification takes place, a part of the product settling and carrying down small quantities of any impurities that have escaped the action of the heat. The sublimed lead is now arrested by forcing the gases and lead into strainers of fine textile fabric, where the gases escape by filtration. The sublimed lead is taken from the strainers and is ready for the market.

The process assures a more intimate combination of the vaporized atoms of the lead and zinc to form a neutral whole in which every atom is approximately of the same physical character and equally affected by any of the causes that injure a paint, than is possible in a pigment formed by a chain of partly chemical and partly mechanical operations acting upon a number of separate substances at different stages of the manufacturing process. Sublimed lead is absolutely free from soluble acids or sulphur, is amorphous, non-crystalline, and fine and smooth in the character of its atoms. Being a pyrogenic-formed substance, it is not affected by heat or deleterious gases of the atmosphere or manufactories; does not turn gray on long exposure to the sunlight, and is not liable to chalk like corroded white lead. Though it dries firm and of almost ivory hardness it does not blister, crack, and peel like the oxide of zinc or mixtures of zinc oxide and corroded white lead. It is elastic, mixes thoroughly with the oil, and dries well without an excessive use of driers, either metallic or liquid. Pound for pound it covers better than white lead, and keeps its color better, as the following comparison of painted boards exposed to furnace gases shows. The action of the weather upon sublimed lead is confined to the surface destruction of the oil vehicle. Rain and wind do not affect or remove the pigment. When the surface of the paint shows decay, the coating can be repainted without removing the old paint. Either the white or blue products of sublimed lead will take a tint more uniformly than is possible with any mixtures of white lead and zinc oxide incorporated by the usual grinding processes.

Fig. 15.—Sublimed lead.

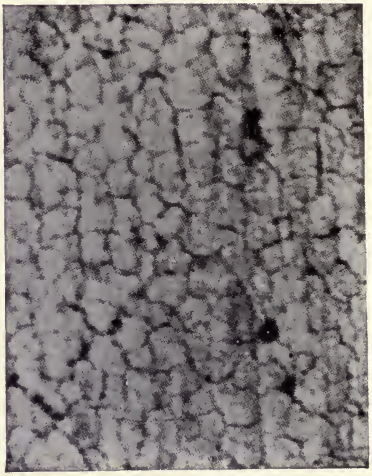

Fig. 16.—Pure corroded white lead.

The cuts are reproductions from a photograph of a picket fence, each alternate picket being painted with the different leads at the same time and by the same painter, using the same oil as a thinner for the pastes, and the same driers, a separate brush being used with each paint. Three coats of each paint were applied, each being allowed to dry thoroughly hard before the next coating was spread. After an exposure of three years and one month the photographs were taken. The cuts are magnified ten times. The chemical reaction between the corroded white lead and the oil forming a lead or paint soap is clearly apparent. The shrinkage of the paint soap has caused the coating to crack. Moisture has entered and loosened the bond of the paint to the covered surface, while the soluble character of the lead soap has caused the whole coating to "craze," and it is ready to fall off by any slight mechanical disturbance.

The sample of sublimed lead shows that no reaction (or but little, if any) has taken place between the sublimed lead and the

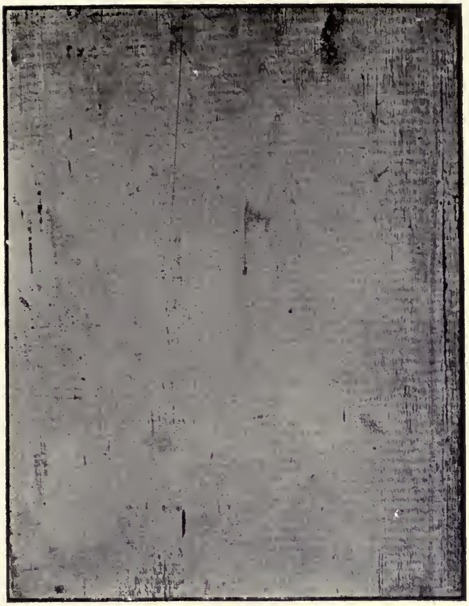

FIG. 17.—Sublimed lead.

FIG. 18.—Pure corroded white lead.

oil, and that the impervious character of the coating has kept out the moisture, and the paint is still firmly bonded to the wood; the streaking being due to the running down of the road dust when wetted by storms, no crazing being noticeable.

Fig. 17, sublimed lead, and Fig. 18, pure corroded white lead, are two-coat applications of the respective paints on a well-seasoned board after an exposure to the atmosphere for three years.

CHAPTER VII.

ZINC OXIDE (ZnO) AND OTHER ZINC PAINTS.

Metallic zinc (Zn), specific gravity, 6.86 cast; 7.14 to 7.20 rolled = 437.5 pounds per cubic foot; combining weight, 65.4; tensile strength, 5000 to 6000 pounds per square inch; electrical conductivity, 29. It melts at 780° F. and begins to volatilize in the open air at 800° to 825° F.

ZINC is electro-positive to copper and iron, whether in solution or in contact. In contact with iron or steel it forms a galvanic pile and decomposes with the evolution of hydrogen. It is used in this form to protect steam-boilers from corrosion. Each pound of zinc decomposed evolves 5.6948 cubic inches of hydrogen that weigh 210.29 grains and develop an electrical or decomposing energy of 1.172 horse-power when used in a sulphuric-acid battery or 1.06 horse-power in a Bunsen or Grove battery.

This electrical energy, while not so strong as in the oxide or salts of zinc in a battery form, is still present, and is recognized by painters as "*movement in the paint,*" which is very marked with zinc pigments, as will be hereafter explained.

Mallett's experiments determined that copper and zinc plates in contact with iron increased the corrosion of the iron 60 per cent. Copper alone in contact with iron, 40 per cent. Elsner found that the oxides of tin, zinc, and iron used together in a paint set up galvanic action enough to crystallize the tin into flakes, which could then be rubbed off.

Zinc is associated with nearly all of the other metals as a mineral ore. It is roasted in special furnaces and by processes similar to those used in the reduction of lead ores for the metal or its oxides. The presence of these associated metals affects the quality and color of the oxides.

The native carbonate of zinc ore, ($Zn.CO_3$) (calamite, zinc spar), *specific gravity* 4.45 *to* 5.0, is found in many parts of the world in heavy beds as crystals, translucent when pure, but tinged more or less gray, green, or brown, according to the other mineral substances associated with it.

Zinc forms but one oxide, ZnO, composed of zinc 80.344 per cent and oxygen 19.656 per cent; *specific gravity*, 5.42.

Zinc oxide is produced by two methods: First, by the oxidation of the metal (French process), which gives a more dense and harder pigment than that prepared by the second method—the sublimation of zinc ore (American process). The product from the first process is preferable for straight oxide-of-zinc paint; the second is better for use in combination with other pigments. Both varieties grind and mix better with poppy-seed oil than with any other vehicle, and manganese-borate drier should be used in preference to lead driers, which are liable to blacken the paint on exposure.

In both processes the zinc is reduced to a vapor by the furnace heat (about 850° F.), and is exposed to a current of air that changes it to a flake, filament, or needle form, according to the care exercised in the process. Some of the particles of the metallic zinc are apt to be carried over in the vapor unchanged, mixed with the atoms of carbon from the reduction fire. These carbon-atoms tend to give a gray color to the product, while the metallic-zinc particles are subject to an attack from the carbonic acid in the atmosphere, forming the zinc carbonate ($ZnCO_3$); this latter change occurring in the pigment after it is mixed into a paste or paint.

The French brand of zinc oxide (La Vielle Montague Co.) is the best in the world, probably, due to the purity of the metallic zinc, the care exercised in its reduction, and by the use of poppy-seed oil, with which the oxide is ground immediately after its formation.

Most of the American zinc ore contains lead, tin, antimony, bismuth, silver, etc., the oxidation of which in the reduction furnace produces white pigments, but they are all blackened by sulphurous hydrogen, which affects the quality of the zinc product, and aids in setting up the electrolytic action that all zinc substances are sensitive to, as before stated. Sulphur is also present in many zinc ores, and causes a yellow color in the oxide.

History of Zinc Oxide.

In 1781 a French chemist discovered the process of reducing zinc to an oxide, and advised its use instead of white lead, but no special results followed.

In 1796 an Englishman patented a zinc-combination pigment, but it did not come into general use against white lead.

In 1844 Leclair, a Frenchman, made zinc oxide and founded the La Vielle Montague Zinc Co. Leclair died in 1872. He received a gold medal from the Society for the Encouragement of the Arts, and was decorated with the Grand Cross of the Legion of Honor for having improved the practice of painters.

Leclair *disguised* the fact of the use of zinc oxide as a pigment. His product was always sold as white lead, a precedent that mixed-paint manufacturers of the present day follow but too well if the analyses of commercial white leads given in Chapter VI are any indication.

The Leclair process consists of volatilizing the metallic zinc in a retort, the vapors as they issue from it being met and mingled with a current of hot air from a blower which completely oxidizes them. The resulting products of combustion are led through a series of flues and chambers, where the zinc oxide is deposited in the form of a flocculent, impalpable white powder ready for use as a pigment.

The American process for the sublimation of zincite ore into zinc oxide was invented by Mr. Samuel T. Jones in 1850, who constructed a furnace for effecting this purpose. This process was improved by Col. Samuel Wetherell for the purpose of working the franklinite ore from the New Jersey deposits.

Wetherell's invention embraced a special furnace and a process. The zinc ores are mixed with pulverized anthracite coal, and charged into a closed furnace having a perforated grate, through which an air-blast furnishes the air necessary for the combustion of the coal and oxidation of the zinc. The vapors from the furnace are led through a number of flues and chambers, where the coarser particles are deposited, while the fine air-floated atoms of the zinc oxide pass on and are collected in a number of fine muslin bags, through which the combustion gases filter away to the atmosphere; the latter part of the process being similar to the Lewis and Bartlett bag process, used in the production of sublimed lead, described in Chapter VI. The franklinite and zincite ore found near Mt. Sterling, N. J., now furnish most of the American zinc oxide.

About 44,000 tons were produced in the United States in 1900, and its use for house-painting is increasing at the rate of about 8 per cent yearly. The New Jersey deposit of zincite is almost absolutely free from lead, antimony, sulphur, and other metals that affect the color and quality of zinc oxide. In France its use has almost superseded white lead for interior house-painting, the Government prohibiting the use of white lead for this purpose.

Zinc oxide made from the ore is used more extensively than that made from the metal. The latter not only dries harder and is more brittle, but on large surfaces the difference in the whiteness of the coatings is very apparent and in favor of the mineral oxide. Zinc oxide mixed with water tends to collect in lumps or masses. It should be thoroughly dry before being ground with the oil. It does not unite so thoroughly with oil as lead or iron pigments, nor dry as quickly.

One-third of one per cent of litharge, added to the linseed-oil in which zinc oxide is ground, renders the paint more elastic and less liable to peel.

Mixtures of zinc oxide, white lead, and ground silex-barytes in the proportions of about one-third each, prove very durable in southern climates and seacoast exposures. The silex gives body to the paint, but being transparent, detracts from its coloring or covering power. There is less white lead in the mixture to saponify with the linseed-oil to form a lead soap that is quickly washed away by storms. The oil also dries out and the white lead is rendered liable to chalk. Such coatings cost less than pure white lead, are more bulky, and by a little extra labor on the painter's part can be made to cover more surface than white lead and zinc oxide, and they save oil.

Zinc oxide 50 per cent, white lead 25 per cent, and Blanc-Fixe 25 per cent, also stand southern and seacoast exposures better than white lead alone. When the above mixtures are used on wooden structures the barytes and silica act as fillers in the first coat, and the percentage of either substance can be greater than in the other coats.

Pure zinc oxide is a pure white pigment but little affected by sulphur fumes, and does not yellow the oil with which it is ground or mixed. It is of itself a good drier, and is used in the preparation of kettle-boiled oil. When it forms the principal pigment in a paint, other driers are detrimental, as the coating has a tendency to harden upon the surface only, and remain viscid below and peel readily. Linseed-oil dries harder than poppy-seed or walnut-oil. In zinc-oxide and white-lead mixtures, more lead than oxide will be required when linseed-oil is the vehicle, in order to keep the coating elastic and avoid its tendency to "craze" or peel.

Zinc oxide carries more oil than white lead, hence spreads better and reduces the tendency of the lead coating to chalk, simply because there is less lead in it and the atoms of each are better coated with the oil from the larger quantity of it necessary with the zinc pigment. Mixed-zinc oxide and white-lead coatings are, in general, more durable than either coating alone, provided both the pigments are pure. As zinc oxide costs more than white lead, the adulteration of it is quite as general, and with the same substances. (See Chapter VI.)

It deteriorates by long keeping and loses much of its covering power, which can be restored by heating the pigment. When freshly made or heated and exposed to moist air, it changes, by absorbing carbonic acid, into the carbonate of zinc ($ZnCO_3$). Painters say "*it spoils,*" and guard against this change by closely covering or sealing it, or mixing it at once into a paste or paint, where the oil protects it, except those particles that lie upon the surface. The carbonate of zinc so formed is crystalline, loses density, and hardens so that it cannot be pulverized or ground without extreme effort.

In this change 81 parts of zinc oxide (ZnO), composed of zinc 80.344 per cent, oxygen 19.656 per cent, specific gravity 5.42, corresponding volume 14.9, are changed to equal 125 parts of the carbonate of zinc ($ZnCO_3$), composed of zinc 52.153 per cent, oxygen 38.278 per cent, carbon 9.569 per cent, specific gravity 4.44, volume 28.1.

This chemical change, attended by so large an increase in volume (nearly double), if it takes place after the oxide has been spread as a paint, the whole coating will be loosened, and the loose particles will be carried away by storms; the action being similar to that which would occur should the sand mixed in the mortar of a plastered wall, when dried, change its volume to the same degree.

Zinc oxide is therefore not a permanent paint for open-air exposures, but for interior use is permanent; for though carbonic acid is present, the moisture is absent, both elements being essential for the change to a carbonate. Dry, gaseous carbonic acid does not affect dry zinc oxide. It is mixed with white lead for interior use to lessen the tendency of the white lead to darken by absorbing the sulphuretted hydrogen present in nearly all locations, a small amount of which darkens the lead pigment. Such coatings are harder than the lead coatings, as the surface has changed in the exposure of drying to a carbonate of zinc.

Zinc oxide is a hazardous pigment to use for external exposures when mixed with iron oxide, lead, or other color pigments. No process of mixing them can so associate the several pigments, even when ground in the oil, as to enable any one particle of either substance to thoroughly protect any particle of the others present, from the changes mentioned. Atmospheric moisture and gases will sooner or later reach the zinc oxide, whether in the first or other coats of the paint, and the inexorable laws of chemical change will govern the durability of the coating, the ultimate decomposition of which will be determined simply by the amount of zinc oxide present.

Zinc sulphate ($ZnSO_4$) is a white pigment, and is often produced in the manufacture of zinc oxide, the color of which is not affected by its presence, even if the sulphate is added to the oxide afterward. Zinc sulphate has recently been brought forward as a desirable pigment for ferric as well as for wooden surfaces. In Germany and England it is used largely in all mixed paints, and has thus far proved to be very resistant to atmospheric influences in damp locations. Like zinc oxide and the lead pigments, its cost is a great factor against its more extended use. The commercial zinc-sulphate paints are adulterated with barytes, the natural composition of which is favorable for its admixture with the sulphate.

Zinc sulphide is a pigment introduced by Mr. J. B. Orr, of England. Its composition is, barium sulphate 70.50 per cent and zinc sulphide 29.50 per cent, the reactions being, $BaS+ZnSO_4=BaSO_4+ZnS$. The dense white precipitate formed is highly heated, then quenched in water, and finely ground and dried. Becton white, Oleum white, Orr's white, etc., are zinc-sulphide pigments. Great purity of the raw materials is required to produce a purely white product.

Zinc sulphide is largely used in the manufacture of enamel paints, linoleum, table oilcloths, etc. It does not continue to oxidize after mixing with linseed-oil, as do lead oxides, and can be considered as a saturated or non-siccative compound. It does not combine with resin, and therefore will not saponify. Exposure affects it by blackening the paint if a lead drier has been used with the linseed-oil, or a lead pigment associated with the sulphide pigment. In these cases a lead sulphide is formed which is dark-colored.

Lithopone or Lithophone is a German paint compound only lately manufactured in the United States. As a commercial mixed paint, it is composed of sulphate of zinc, zinc oxide, and barytes or Blanc-Fixe, generally, one-third of each substance, and is similar in character to Charlton's white and Griffith's patent zinc oxide. It is commercially classed as Green Seal, Red Seal, Blue Seal, and Yellow Seal. The Green Seal consists of one part zinc sulphate and two parts of barytes. The Red Seal, of one part zinc sulphate and three parts of barytes. The specific gravity of the Red Seal is 4.2. The Blue and Yellow Seals contain some zinc oxide with the sulphate, and a greater percentage of barytes, and are consequently deficient in covering power. The large amount of oil taken up by the sulphate and zinc oxide is counteracted by the smaller quantity taken up by the barytes.

Barytes costs about one-tenth as much as zinc oxide or zinc sulphate, and affords every requisite to grade up the weight of zinc paints, even when a liberal amount of whiting is present, as is too frequently the case with most mixed pastes or color paints. (See Tests of Paints.)

Green-seal lithopone approaches closely the best brands of French zinc oxide, and does not require so large an amount of thinners as the American brands of zinc white, and it works easier. It is unaffected by sulphurous gases, and does not turn yellow when thinned. It will blacken if exposed to the sun before it is dry. Oils or driers containing lead or copper salts turn lithopone gray; neither can it be used with other colors having a lead or copper base.

Griffith's zinc white, a chloride or sulphate of zinc, is precipitated from a soluble sulphide or chloride of sodium, barium, or calcium. No iron should be present. The precipitate is dried, and then calcined at a low or cherry heat, with careful stirring; raked out of the furnace and quenched in vats of cold water, then levigated and ground. It is an oxysulphide of zinc; some sulphate of magnesia accompanies the pigment.

A commercial zinc white that is only a sulphate of zinc is made by precipitating the pigment, by the addition of a dilute solution of sulphuric acid, to an acetic- or nitric-acid solution of litharge. Wash and dry the precipitate thoroughly. The clear liquor can be used repeatedly. All of the metals associated with the zinc in the litharge are dissolved by the nitric or acetic acids and precipitated with them as sulphates, and are inclined to blacken on atmospheric exposure. The zinc pigments formed by the precipitation processes are not as durable or reliable as those formed by the oxidation or sublimation processes from metallic zinc or the zinc ores.

A mixture of one part of zinc oxide with two parts of red lead has given very satisfactory results in retarding marine corrosion in both salt and fresh water.*

The United States Bureau of Construction specifies one part of white lead to three parts of zinc oxide for the paint used on wooden structures on the seacoast, and has lately abandoned the use of zinc-oxide pigments on ferric structures wherever located. House-painters use from 20 to 50 per cent of zinc oxide when they mix their own colors. The great percentage of zinc oxide in the commercial mixed-white paints and colors has been referred to in Chapter VI.

Adulterations of Zinc Oxide, and Tests.

Patent zinc white is a sulphide of zinc mixed with baryta or strontia. Fulton's zinc white is the sulphide of zinc and barytes. Charlton's zinc white is the same.

In the adulterations of zinc oxide with baryta, barytic white, permanent white, Blanc-Fixe, constant white, etc., all of these substances are artificial sulphates of baryta, and are less crystalline than the natural sulphate, and cover better. Pure zinc oxide dissolves entirely in dilute sulphuric acid, leaving no residue. If carbonate of lime is present, it effervesces with muriatic acid, and the amount of this action in a measure indicates the amount of that adulterant present.

Zinc oxide lacks weight when compared with white lead for paint mixtures. Barytes in its powdered form supplies this deficiency, but has poor covering power; it spreads well and saves oil. The floated barytes—a finer grade floated from the pulverized natural mineral—has better covering power than the ordinary brands of this pigment, simply because it is finer. Artificial barytes or "Blanc-Fixe" frequently contains pulverized silica or white-glass sand. All of these substances are adulterants, and add nothing to the qualities of zinc oxide except weight and a saving of oil that lessens the cost of the mixture to the manufacturer, but seldom to the consumer.

To test a mixed zinc-oxide paste or paint for adulterations, repeated washings with benzine or ether will remove the oil; then dry the residuum on blotting-paper. Dilute sulphuric acid completely dissolves zinc oxide, leaving the adulteration or any other metallic-base pigments unaffected.

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* "United States Navy Yard Tests of Marine Paints," Transactions American Society Mechanical Engineers, Vol. XVI, 1894. Paper Number 625, p. 390.

A dilute solution of muriatic acid will dissolve the lime, if any is present. The barytes, silica, etc., will remain after the residuum has been ignited.

On a painted surface, slightly scratch the coating, and apply a drop of sodium sulphide of 100° Baumé. If lead pigments are present a discoloration will follow the application of the sodium.

CHAPTER VIII.

LAMPBLACK.

The carbon group of pigments comprises lampblack, mineral or natural asphaltum, artificial asphalt, coal-tar, and graphite, either alone or as a component part of the paint.

Lampblack is the fine deposit or soot formed by the imperfect combustion of oil or fatty substances. Its composition varies greatly, depending upon the nature of the substance consumed in its formation, and the care exercised in the combustion process. Fatty oils and grease yield the best lampblack. Coal-tar yields a black of a brownish hue and is inclined to be oily. Resin furnishes a good black. If the combustion is forced it carries along some of the free resin-flakes, and yields a yellowish resinous black of an inferior quality, not always free from grit and dirt.

Gas-black, the soot product from the combustion of hydrocarbon fuel or illuminating coal-gas, differs in molecular structure from the fatty-oil blacks. The gas-black particles appear to have a star form, and are not as suitable for mixing with white lead or zinc white for tints as the fatty-oil blacks, though their color is densely opaque. The fatty-oil lampblack is filament-formed, and incorporates with the oil and oxide pigments better than the star or flake-formed blacks. Gas-black is also made from natural gas burned under revolving cylinders, the deposited soot being removed by scraping. With proper care the lampblack so formed is nearly pure carbon. In a paint coating it has a tendency to become brittle, crack, and flake off after a short time. This possibly results from using too much drier or turpentine in the vehicle, as of itself it is a slow-drying pigment, and adds no drying qualities to the vehicle. It seldom appears in the market as gas-black.

Ground soot appears as a lampblack under various trade-names. It contains ammonia, sulphuric and pyroligneous acids, rain-water, and carbonic acid. Under atmospheric conditions, solutions of these acids are produced strong enough to set up galvanic action on roofing material and ferric surfaces. With galvanized iron or sheet zinc, the zinc is reduced to either an oxide, sulphate, or carbonate at the expense of the zinc covering, leaving the iron exposed to the action of the elements which produce corrosion, that is the more active because of the galvanic couple of the different metals. (See Galvanizing, Chapter XVII.)

Spanish black, or cork-black, is made from the combustion gases of burning cork. It is a good lampblack in color and texture if proper care be taken in the process; but charred cork and ashes are too often present in the product for its good.

Ivory-black is made from chips of elephants' tusks and other hard bones free from fat. It should have no lustre, as that indicates the presence of unconsumed fatty matter. Its use is almost exclusively for the preparation of the finest blacks for carriage, decorative, and artists' colors. Its high cost debars it for use in ferric coatings.

Horn-black, or animal black, is almost identical with bone-black, but is generally in a more finely divided state. Animal refuse, albumen, gelatine, horn and hoof shavings, etc., are subjected to a dry distillation in a still or retort; the black carbonaceous mass left is washed with water and powdered in a mill. It requires about one and a quarter its own weight of oil for a paste. The great quantity of oil left in the black as it comes from the still is the reason for its slow drying. It is a cold, mild black, and when not well burned has a brown tint, dries badly, and is used for printers' ink, blacking, etc., also for the cheaper grade of black varnishes and paints.

Bone-black, made from a poorer quality of bones than ivory-black, is a warm, reddish-brown black.

Drop-black is an ivory- or bone-black blued with Prussian blue.

Charcoal-black is a finely powdered beechwood charcoal, made in Sweden, and generally marketed as Swedish black. It is a pure black in color, but has less covering power than the fatty-oil blacks.

Blue-black, made from vine-stems, is a better quality of charcoal-black.

Frankfort black, or vine-black, is made from the charcoal left from the calcination of dried vine twigs, wine lees, peach-stones, bone and horn shavings, etc., and contains potash. It varies in shade according as the animal or vegetable charcoal is in excess. The animal matter gives it a brownish hue, the vegetable a bluish color; both have a good covering power. The finest qualities of this black come from the condensed gases as soot in the calcination of the above substances. Many other process blacks are sold under the above names.

Almond-black is made from fruit stones, nuts, etc. It is an intense black, and has the same qualities as Frankfort black.

German black is made from the combustion gases of any resinous matter, which escape into a long flue, at the end of which is a woollen or other fibre hood, that collects the deposited soot.

English black is collected from the flues of bituminous coke-ovens.

Russian black is made from the soot of resinous dead fir- or pine-wood. It is liable to spontaneous combustion if left for a short time moistened with oil.

Prussian black, Berlin black, ochre-black, coffee-black, earth-black, lake-black, paper-black, and manganese-black are all inferior qualities of lampblack made by some one of the many processes, and from the many substances capable of slow and imperfect or smoldering combustion. Their color and qualities are quite as divergent as their names; all dry slowly with uncertain results in color and lustre.

Graphite-black, or ship's black, is an impure lampblack mixed with an inferior quality of flake-graphite, and can be known by its metallic lustre.

Coal- or *shale-blacks* are generally pulverized slaty bituminous coal.

The trade adulterants of lampblack consist not only of those substances that in the process of manufacture are imperfectly carbonized or vaporized, but nearly every other light substance that is black and can be ground to the required fineness. The coarse soot and scales deposited in the chimneys and flues from the combustion of fatty-wood and soft-coal fires, coal-gas, mineral oil, shale, and asphaltum, coal-tar, etc., in the several processes of distillation or burning for other products, all contain ashes; also acetic, pyroligneous, and sulphuric acids, ammonia, and tar to a notable extent, that condense in the carbon-atoms, and materially affect the color and quality of the lampblack. These are not always removed in the subsequent calcination that all lampblacks require to form the prime pure product known as "burnt lampblack." These acids and the tar prevent the drying of any lampblack coating, except by the use of an excessive amount of strong driers. In such cases the paint hardens only on the surface, and remains viscid underneath, and is prone to peel.

Anthracite and bituminous coals are ground and marketed as pure lampblack. They contain from 8 to 12 per cent of ash, also from ½ to 2 per cent of sulphur, and absolutely have not a single quality to recommend their use except their low price. From the large quantity of worthless lampblack selected for the finishing coating of most of the ironwork in the New York Rapid Transit Subway, it might well receive a special trade-name as the "Subway or Tunnel black."

Carbon-black appears in the market as hydrocarbon-black, American gas-black, satin-black, gloss-black, jet-black, silicate of carbon, etc.

To make a pure lampblack requires not only a proper material, but as careful attention to the combustion of it and the subsequent processes for its preparation as the manufacture of any other pigment.

Pure lampblack made from a fatty oil is so finely subdivided naturally, that it requires no grinding. It is only ground in the vehicle to secure a more thorough incorporation than is possible by stirring it in. It is of an oily feel and nature, and in combination with a good oil forms a more elastic and closer-clinging coating than any other pigment.

It is chemically and electrically passive, non-hygroscopic, non-corrosive, and less affected by heat, light, and peeling than any other pigment.

Its life in a paint coating is in a great measure exempt from all atmospheric influences that cause the decay of a paint. Its elastic nature reduces the frictional element due to the beating of storms, while the oxidation or decomposition of organic matter in the dust and from other sources is almost *nil.* It remains in place until removed by friction or the destruction of the vehicle, and can be painted over without the expensive torch-burning or scraping so necessary with other pigment coatings.

In some form or degree of purity lampblack enters into all of the black varnishes, enamels, and trade paints that have any marked quality for the protection of metallic or other surfaces. From its finely divided state and oily nature it is liable to spontaneous combustion, hence must be stored in small bulk and kept well covered. Lampblack requires more than double its own weight of oil to secure a good coating; it is easily brushed out with but small wear of the brushes. Driers added to lampblack paste or varnishes should be in the form of japans, rather than turpentine, which flattens the lustre of the coating.

Many instances are on record where a single coat of lampblack, like that used for the lettering and symbols on the old cross-road and tavern sign-boards, that have been exposed for a century or more, are still uninjured, while the surrounding colors and in many cases the wooden surface of the sign have been worn away, leaving the carbon lettering in full relief.

The iron-link-chain suspension bridge over the Merrimac River at Newburyport, Mass., was made of Norway cold-blast iron, and erected in 1810. It was painted with two coats of pure lampblack and raw linseed-oil over sixty years ago, and is still (1903) practically free from corrosion, though in an exposed position, subject to sea air and fog influences for days in succession.

The use of lampblack to delay the "setting" of red lead is fully described in the article on red lead. It does not, however, prevent the failure of red-lead coatings when they are exposed to the action of hydric-sulphide fumes, but is not itself affected by them.

A good test of the quality of a lampblack is to place the sample on a piece of blotting-paper and pour a little ether on it until the paper is soaked with the ether, percolating through the black. If on the evaporation of the volatile and removal of the powder the under side of the paper appears fatty, the lampblack is of poor quality.

Animal charcoal and bone-black or ivory-black are strong bleaching agents, and it is possible for them to uncolor overlying coatings. The oil protects them somewhat from this bleaching influence, but where long stability of color or lustre is required, it is better to use blacks not of an animal nature.

CHAPTER IX.

MINERAL OR NATURAL ASPHALTUM.—ARTIFICIAL ASPHALT (WHICH INCLUDES COAL-TAR AND ITS PRODUCTS, PITCH, MINERAL WAXES, ETC.).

Mineral or natural asphaltum. There are a large number of these, known as Egyptian, Bermudez, Trinidad, Mexican, Cuban, Californian, Chinese, etc. They all vary greatly in character and purity, and are the residual products of petroleum when the light hydrocarbon elements have been evaporated by natural causes. They contain vegetable and mineral matter, sulphuric and other acids that must be removed by boiling or distillation to render them suitable for enamels, varnishes, or paints. Asphaltum is not to be confounded with the product of coal-tar distillation, called "asphalt," which, having a certain resemblance to the natural asphaltum in some of its physical qualities, is chemically very unlike it. The name asphalt being carelessly applied to both the natural and artificial or coal-tar product, naturally leads to some confusion on the subject. They are, in fact, so widely apart in all their essential qualities that they cannot be appropriately coupled together as relating to the same substance.

The characteristics of asphaltum used for ferric coatings are briefly given: Asphalt, bitumen, or mineral pitch, *specific gravity* 1 to 1.68, softens at 170° F. and melts at 212° F. (coal-tar asphalt softens at 115° F.). According to Boussingault (*Am. Ch. Phys.* [2], XIV, 141) it is a mixture of two definite substances, viz.: *asphaltene,* which is fixed and soluble in alcohol; and *petrolene,* which is oily and volatile. The greater part of the latter may be volatilized by distilling the asphalt with water. The chemical composition of bitumen is:

Carbon.......	85 per cent.
Hydrogen....	12 " "
Oxygen......	3 " "
	100 " "

It is therefore an oxygenated hydrocarburet.

It is the *petrolene* that gives the cementitious or bonding value to compositions into which it enters. Bermudez asphalt is about 2 to 3 per cent purer than Trinidad. Samples of Bermudez analyze 97.22 per cent of materials soluble in bisulphide of carbon. A large amount of these materials is also soluble in ether, showing that the bitumen contains large amounts of petrolene.

Petrolene in Bermudez = 81.63.
" " Trinidad = 80.01.

Egyptian asphalt is the purest of all the varieties of asphalt, but is not procurable at present in commercial quantities required for pavements or paints, but is used in the finer qualities of japanned or enamelled wares, baked coatings, varnishes, etc. Samples of it frequently analyze 99.5 per cent of soluble matter.

Asphaltum yields by dry distillation a yellow oil, consisting of hydrocarbons mixed with a small quantity of oxidized matter. It begins to boil at 90° C., but gradually rises to 250° C., giving oils of specific gravity during the boiling, viz. from 90° C. to 200° C., specific gravity = 0.817 (at 15° C.); that which boils between 200° C. and 250° C., specific gravity = 0.868 (at 15° C.); both portions giving by analysis 87.5 carbon, 11.6 hydrogen, and 0.9 oxygen, which is nearly the composition of the oil of amber.

These asphaltum oils, treated with sulphuric acid and then washed with potash and subjected to dry distillation, yield a number of oils which are *insoluble* in water, or strong nitric acid, and are but little affected by strong sulphuric acid, but are very soluble in alcohol or ether.

Asphaltum has no metallic base, and can be classed as a gum or resin, hence but a small amount of it can be incorporated into an oil vehicle for use as a paint. Bisulphide of carbon and benzine usually form a large percentage of all vehicles in asphaltum paints.

The principal merit of some of these paints consists more in the name than the quality. If it is once considered that only about 10 per cent of asphaltum enters into the composition of the well-known street pavements, and that so little quantity as this amount, however it may govern the other constituents of the paving compound, has to be put in place or applied hot, and cannot be used or compounded in any other manner, it may be apparent that, notwithstanding the catchpenny name, really but little if any asphaltum of either high or low degree ever enters into the composition of any of these paints.

Analyses of many of these paints show that there is not 5 per cent of asphaltum in the composition of any brand of such paint upon the market. Even with this small amount, and with the best of boiled or raw linseed-oil as the vehicle, the paint is difficult to dry without the use of strong metallic salts mixed with the oil to aid its oxidizing or drying quality; and if a quick-drying paint is wanted, these oxidizing materials are added in such amounts as to materially affect the life of the paint.

When the color of the paint is other than black or steely gray, it may be doubted if any asphalt will be found present under the closest analysis; and the red and brown colored samples will be found to rely almost wholly upon oxide of iron as the base of the pigment, under whatever name it may be masked.

Gilsonite, a mineral resin associated with natural asphaltum, is used largely as the principal pigment in these paints. Gilsonite, asphaltum, petroleum, cannel and bituminous coal and shale, all shade off into each other so gradually, and form so numerous a class of bituminous mineral substances, that it is difficult to determine their exact relations. The fluid elements of the hydrocarbons evaporate, and as the heavier portions solidify, they oxidize with a loss of hydrogen, and change until over a hundred different bituminous mineral substances can be determined from the hydrocarbon group.

The general composition of the numerous class of petroleums, after the evaporation of the lightest hydrocarbons by nature in the form of natural gas, is, viz.:

Crude Oil. 26° Baumé. Distillates. Commercial Names.	Approximate Degree. Baumé.	Specific Gravity.	Weight of 1 U. S. Gall. in Pounds.	Percentage Obtained. Approximate.
Gasoline.	75–76	0.6820	5.69	3–5
Benzine.	63	0.7253	6.04	4–6
Kerosene (illuminating-oil).	45	0.80	6.66	13–15
Heavy kerosene (mineral sperm).	38–40	0.8333	6.94	8–56
Gas distillate.	28	0.8866	7.38	10–18
Light lubricating (spindle-oil).	26	0.8974	7.48	8–10
Neutral oil.	23	0.915	7.62	10–12
Heavy lubricating-oil.	21	0.9271	7.72	5–6
Valve lubricating-oil.	14–15	0.9655	8.04	4–5
Asphalt (crude), containing 4 to 7 per cent of sulphur.	11–6	1 to 1.60	8.344 to 13.350	11–12
Loss.	. . . . .	. . . .	. . . .	5 to 13

Other samples of petroleum range from 5° to 6° Baumé higher, and carry more hydrocarbons of the paraffin series.

The illuminating parts of these oils carry more carbon, and less hydrogen, and give a smoky flame, due to the fact that it requires more oxygen to effect complete combustion of the carbon element than it does to consume the hydrogen.

Coal-tar is a generic term applied to those bitumens which are extracted during the destructive distillation of bituminous coal for gas or coke. Commercially, the name is also applied to water-gas tar. The nature of the tar varies with the nature of the coal, and with the processes employed in its production as a waste product in the manufacture of gas or hard coke.

There is no known method of describing accurately the true composition of the coal-tars. No two are identical in every respect, although many are identical in every essential respect. Variations also occur from the admixture with the coal in process of distillation, of greater or less quantities of oils of various kinds, used for the purpose of enriching the gas. The tars vary in the amount of bitumen they contain within the limits of 60 to 92 per cent; also vary largely in the percentages of oil which they contain, and in the quality of the oil. The non-bituminous matter in the tar is generally carbon, which is synonymous with lampblack, and was, of course, a hydrocarbon before the hydrogen was eliminated by combustion. Coal-tar cement, or asphalt, is a residue from the distillation of coal-tar. Its hardness or flexibility is due to the percentage of the oil left in it, and may vary from 16 per cent in one quality of coal-tar to 52 per cent in another. One per cent of oil taken from one coal-tar will produce a greater hardening effect than 1½ per cent taken from another tar, and the degree of heat necessary for distilling off the oil may vary from 200° to 600° F., even when supplemented by mechanical agitation, or by blowing superheated steam or air into the still during the distillation process.

The average analyses of a large number of samples of coal-tar from coal-gas retorts gave for a 40-gallon barrel, *specific gravity* 1.08–1.10:

1½ gals., or 3.75%, of light oils, consisting of benzole, naphtha, and carbolic acid.
9½ gals., or 23.75%, of heavy oil, consisting of creosote-oil and anthracine, etc.
29 gals., or 72.5%, pitch.

Boiled in open kettles, this tar should be reduced from 15 per cent to 25 per cent, according to the duty required of it. The tar resulting from the distillation of petroleum oils for water-gas is of a decidedly inferior quality to that obtained from gas-coals, and is better adapted for coating the cruder forms of wood constructions, piles, dock-timbers, fence-posts in the ground part, than metal-work. But this same oil-tar, if distilled at heats from 600° to 800° F., forms a pitch of almost adamantine hardness when cold, and resists almost all corrosive agents and solvents except those of the hydrocarbon class.

Analysis of a by-product coke-oven tar:

Naphthalene	12.00 per cent
Anthracine	0.30 " "
Tar acids	7.00 " "
Tar bases	1.60 " "
Water	2.00 " "
Pitch	77.10 " "
	100.00 " "

When the concentration of the gas coal-tar is carried to the 25 per cent or 30 per cent stage, the product is comparatively odorless, or at least is not any more objectionable than that from oil paint, the pungency due to the light oils and carbolic acid being dissipated. In the distillation of coal-tar, until the final residuum of coke is reached in the still, there are no constituent oils derived from the process that do not gradually volatilize by the heat of the sun or approximating temperatures; and all coal-tar or hydrocarbon products suitable for use in, or as paints, also become fluid when exposed to heat; in fact, but few of them are applied in any other condition than while hot. They are all liable to run on vertical or slightly inclined surfaces, until by evaporation they are so advanced on the road to brittleness that they solidify, and by a little further progress in the same direction they become brittle and scale off on the least mechanical disturbance.

In the production of an ordinary standard roofing-pitch from a coke-oven tar, the distillation ran, viz.:

Water	1.49 per cent
Light oil (to 325° F.)	3.04 " "
Heavy oil (above 325° F.)	21.47 " "
Pitch (at 585° F.)	74.00 " "
	100.00 " "

The pitch contained about 12 per cent of free carbon. Coal-tar asphalt softens at 115° F. Natural or mineral asphalt softens at 150° to 170° F.

Analysis of a standard coal-gas tar (specific gravity 1.24):

Carbon	89.21 per cent
Hydrogen	4.95 " "
Nitrogen	1.05 " "
Oxygen	4.23 " "
Ash	trace
Volatile sulphur	0.56 " "
	100.00 " "

In combustion it gave British thermal units 15.781. Evaporative power from and at 212° F. = 16.4 pounds of water.

Analysis of water-gas tar from gas-oil (specific gravity 1.15):

Carbon	92.70 per cent
Hydrogen	6.13 " "
Nitrogen	0.11 " "
Oxygen	0.69 " "
Ash	trace
Volatile sulphur	0.37 " "
	100.00 " "

In combustion it gave British thermal units 17.193. Evaporative power from and at 212° F. = 17.8 pounds of water.

In the distillation of an oil water-gas tar by Dr. John F. Wing, the products obtained at the several stages of the process were as follows (specific gravity of the crude tar 13.5° Baumé = 1.1—water 1):

Distillation heat, F.	Percentage of distillate.
240° F. water	0.25 per cent
240° F. light oil	4.25 " "
240° to 336°	0.50 " "
336° " 400°	3.00 " "
400° to 550°	29.00 " "
550° " 617°	5.00 " "
617° " 690°	17.00 " "
Above 700° a hard-pitch residue	41.00 " "
	100.00 " "

At 400° F. the distillate became heavier than water. The residues obtained at temperatures of 550° to 617° F. were soft pitch, but would not flow. There were from 12 to 15 per cent of free carbon in the oil-gas tar, while 5 to 8 per cent are the usual amounts found in an Otto-Hoffman coke-oven coal-tar.

The acids and ammonia salts in crude coal-tar must be eliminated by boiling or distillation when used for coating ferric bodies. If they are not removed, the tar, either hot or cold, is one of the most unreliable and unmanageable of coatings. (See Dr. Angus Smith's experience, Chapter XII.)

The mineral waxes derived from coal-tar are the most reliable of all the coal-tar paint products. They are especially not affected by "sweating." They are an intermediary substance between the fluid and volatile elements and the heavy ones; and retain some of the volatile element that, as it slowly evaporates, causes the paraffin to crack badly and change its volume. The spaces between the tension-chord and other eye-bars in modern bridge constructions, lying so closely together as to be incapable of inspection or repainting to protect them from corrosion, are often filled in with melted paraffin as a protection from rust. It requires but a short period for the wax to harden, shrink, and crack, and expose the ferric bars. As well expect a cracked varnish coating to protect the surface it covers, as one of cracked paraffin.

CHAPTER X.

ASPHALTUM PAINTS AND CARBON VARNISHES.

ASPHALTUM paints are proprietary products, and vary in composition and quality quite as much as does the substance from which they derive their name. There is no standard of excellence in asphaltum paints.

A small amount of some quality of mineral asphaltum or gilsonite, mixed with varying amounts and qualities of the trade lampblacks, constitutes the pigment for the numerous brands of quick-drying paints used to blacken a large class of ferric bodies that need a coating for appearance rather than protection from corrosion. The catchy name often secures their use on more important structures, where the price at which they are offered should promptly condemn them before trial.

A supposed better class of asphaltum paints or so-called varnishes, similar to the "Maltha," "P. & B.," and other trade-mark designations, are freely marketed as superior paint products. They are in no sense varnishes, but simply the above-mentioned class of pigment substances, mixed with bisulphide of carbon, benzine, and other uncertain hydrocarbon liquids and oils, the latter often containing more resin-oil than linseed-oil. They are not compounded by heat, as all true varnishes are. They have had an extended trial for over fifty years on important ferric structures,—naval, hydraulic, and other work, only to fail after a brief exposure. Wherever placed in competition with other carbon or metallic-base coatings they are invariably found low in the column of merit. As a rule they spread easily and show well at first, but when the volatiles have evaporated, especially if they have been subjected to a moderate heat test 140° to 180° F., they become brittle, turn brown, crumble, and are easily removed. The application of these paints, containing bisulphide of carbon, is attended with extreme danger from fire, even on external exposures. The vapor of bisulphide is very explosive at low temperatures, also disastrously injurious to the painters or others breathing it during the application of the paint in any confined space, and only moderately less so in the open air.

Fig. 20.—Animi Fossil Resin.

An account of its application to water-mains, where it resulted in the insanity and death of a number of the painters and workmen engaged in painting and laying the pipes; also in the utter failure of the coating to protect the same pipes from corrosion, is given in "Transactions American Society Mechanical Engineers," Vol. XVI, 1895, Paper 637. Also in *Engineering News*, Feb. 7, 1895, and April 4, 1895.

A further demonstration of the inferiority of these asphaltum paints in competition with other oil paints and black varnishes is given in a series of tests made by Mr. Max Toltz, C.E. The Report was read before the Society of Civil Engineers, St. Paul, Minn., and reported in the *Journal of the Association of Engineering Societies*, 1897. It was also briefly referred to in "Transactions American Society Mechanical Engineers," May, 1901. (See also Bisulphide of Carbon, Chapter XX.)

Asphaltum varnishes or carbon paints in which the vehicle is practically a linseed-oil varnish, compounded by heat, and of the same nature as a baked-japan vehicle in which the carbon-blacks and other pigments are ground, are very reliable for protective coatings. They seldom fail under the severest tests of marine or other corrosive exposures.

Fossil Resins.

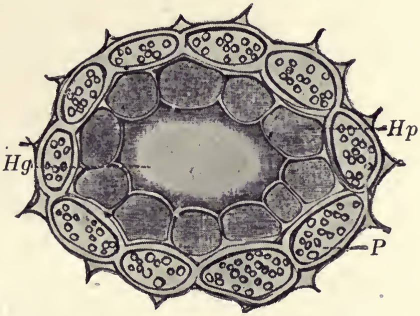

FIG. 19.—Section through a resin passage of *Abies excelsa* (fir- and spruce-trees). The cavity *Hg*, as well as the thin-walled cells *Hp*, are filled with semi-fluid resin. The thick-walled cells *P* contain starch.

Fossil gums or resins, under the general name of Copals, are those used for varnishes or varnish paints. They are incorporated by heat with refined linseed-oil, and when black generally contain a quantity of the better class of refined asphaltum.

The oldest and hardest of the fossil resins is Zanzibar; the trees that furnished it are extinct.

There are about thirty different resins used in paint and varnish manufacture, many of them possessing peculiar qualities. The best are the fossil resins found in the beds of rivers or in the earth where they have lain for centuries. The hardness of these fossil gums appears to depend upon their age and the pressure that they have undergone while buried. *Amber* is the hardest and most valuable of all resins. Only the refuse of black amber is used for varnish. Amber varnish merely means *amber-colored* varnish. There is no amber in the commercial brands.

Copal is the next in hardness; it comes from Zanzibar, and is known in the English trade as "Animi," from the insects embedded in it. Being very difficult to dissolve, it is distilled until it loses from 20 to 25 per cent, when it can be dissolved in boiling oil. There are three varieties of it, and many grades.

"Animi" is now the technical name for the South-American copal, and comes from Brazil.

Sierra Leone copal has nothing to do with Sierra Leone except for its name. It comes from the river-beds in the interior of Africa. It is the only African resin that will dissolve in cold alcohol. Its color is not as good as the Zanzibar or best Kauri, but it is harder than the Kauri. It is mixed with the Zanzibar for hardness, itself giving toughness to other fossil resins.

Other African copals are the Pebble or Pebble-stone—which is the hardest—Acora, Loango, Gaboon, Congo, Benguela, and three sorts of Angola.

Manila is of two kinds,—a hard and a soft; neither are fossil gums. They come from the Philippine and other islands, Borneo, Singapore, etc. This gum can be used as it comes from the living tree like the crude resin from the American long-leaf pine.

Dammar is a recent resin from trees not extinct, and contains the most water. When it forms the principal resin in a varnish or varnish paint, it appears to be always drying, hence the danger to any other coating spread over it. It is the resin used with enamel paints to give the high gloss characteristic of these coatings.

Sandarach is a resin yielded by the barberry-trees of Northern Africa. It is used to a considerable extent as the basis of spirit varnishes.

Kauri or *Cowrie*, from New Zealand, is the principal fossil resin used for a varnish, being about ten times the amount of all the other resins combined. It is produced from a species of tree not yet extinct, but the gum as it exudes from the tree at the present day is of no more value for a varnish than that from the common spruce-tree; but when it has lain in the earth for centuries it becomes hard and valuable. It is very indifferent to the action of sulphur gases, and is more colorless than the other fossil resins. It is easily dissolved, and melts more readily than mastic, but less so than the common resins. It is allied in composition to Dammar resin, and is from two to nine times cheaper than the other fossil resins whose prices range in the order of commercial quantities as follows:

		Prices per pound.
First.	Kauri	10 to 50 cents.
Second.	Manila	10 “ 25 “
Third.	Dammar	16 “ 25 “
Fourth.	Zanzibar, best	$1 “ $1.25
Fifth.	Benguela	85 “ 90 cents.

The general composition of all fossil or other resins is $C_{20}H_{40}O_2$. Their specific gravities at 60° F. are:

Yellow-leaf pine-resin (dark colophony)	1.100
“ “ “ “ (whitish opaque)	1.047 to 1.044
“ “ “ “ (yellow transparent)	1.084 “ 1.083
Shellac, D. C. (dark colored)	1.123
“ L. C. (light colored)	1.114 “ 1.113
“ B. (bleached)	0.968 “ 0.965
Copal, East Indian	1.070 “ 1.063
“ West Indian	1.080 “ 1.070
“ Very old	1.055 “ 1.054
“ Zanzibar	1.068 “ 1.067
Dammar, Manila	1.121 “ 1.062
“ old	1.075
Benzoin, Siam	1.235
“ Penang	1.155 “ 1.145
“ Borneo	1.170 “ 1.165
Guaiacum, pure	1.237 “ 1.236
Tolu, old and brittle	1.232 “ 1.231
Amber	1.094 “ 1.074
Sandarach	1.044 “ 1.038
Mastic	1.060 “ 1.056
Angola	1.081 “ 1.064
Kauri (Australian)	1.115 “ 1.050
Brazilian	1.082 “ 1.018

Shellac is an animal resin produced from the banyan- or fig-tree and other trees of India, called "Lac-trees." Lac is the root of the word Lacquer, of Indian derivation, and was probably first applied to specimens of Chinese lacquer-ware, imported through India. The branches of the lac-trees, when stung by the female insect *Coccus-lacca,* exudes a sap that the insect transforms by digestion into a resinous excretion (lac), with which she encrusts her eggs and herself. The insect is indigenous to the forests of India. The exudation of the sap from the lac-tree is somewhat similar to that produced by an insect or parasitic fungus on a species of oak (the gall-oak) that produces the "gall-nut" used by dyers and in pharmacy. The lac, when sent to market, often contains the eggs of the insect, and is called "seed-lac."

The lac secretion is dissolved from the twigs and branches of the tree in hot water, the solution is then evaporated on hot revolving cylinders, or in shallow pans, then scraped off in the form of thin sheets, broken up, and forms the commercial shellac, graded generally as D. C. (dark colored), L. C. (light colored), B. (bleached), etc.

The coarse qualities of the melted lac, when dropped into rounded pieces 1 to 1½ inches in diameter, are called "button-lac," and when in larger pieces are known as sheet-lac or "piece-lac."

The best quality is *kusum-lac,* from the *kusum* tree (*Schleichera-trijnga*), which lasts about ten years after being stung. The twigs from this tree are of a light-golden color and furnish the orange shellac; coming principally from Siam. The second quality is furnished by the *dhak* or *palas,* from the *Butea frondosa.* The third quality is the *pipal,* from the *Fiscus religiosa.* All of the lac-trees except the kusum live only from two to three years after being stung by the insect. Commercial shellacs are extremely variable in quality and price. The best grade of fine Orange D. C. lac brings £10 12*s.* per cwt. in London; "Native Orange," £8 9*s.* per cwt.; "Garnet," £7 8*s.*; "Native leaf" and "Button," £3 8*s.* to £3 6*s.*

The composition of shellac is given by Mr. Halstead* as

	Stick-lac.	Seed-lac.	Shellac.
Resin................	68.00 per cent.	88.50 per cent.	90.90 per cent.
Coloring-matter.......	10.00 " "	2.50 " "	0.50 " "
Wax..................	6.00 " "	4.50 " "	4.00 " "
Gluten................	5.50 " "	2.00 " "	0.00 " "
Extraneous and nitrogenous substances...	6.50 " "	1.00 " "	2.80 " "
Loss.................	4.00 " "	1.50 " "	1.80 " "
	100.00 per cent.	100.00 per cent.	100.00 per cent.

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* Geo. Watts's Dictionary of the Economic Plants of India. Government Printing-office, Calcutta, 1889.

A more complete analysis by Dr. Johns* shows that 120 parts of stick-lac consist of

An odorless common resin	80.00 parts
A resin insoluble in ether	20.00 "
Coloring-matter analogous to cochineal	4.50 "
Bitter balsamic matter	3.00 "
Dun-colored extract	0.50 "
Acia (laccic acid)	0.75 "
Fatty matter like wax	3.00 "
Skins of the insect and coloring-matter (the latter furnishing food for the grub when hatched)	2.50 "
Salts	1.25 "
Earths	0.75 "
Loss	3.75 "
	120.00 "

Shellac dissolves readily in alcohol, benzine, muriatic and acetic acids, but not in concentrated sulphuric acid. It dries solely by the evaporation of the solvent, leaving the thin film unchanged, the only use of the solvent being to spread the varnish. When alcohol is used as the solvent, the varnish can be spread over damp surfaces, as the alcohol will take up the moisture without much apparent injury to the coating, though this will be longer in drying, as the water must be evaporated with the alcohol.

Shellac can be applied to ferric surfaces, and in under-water (fresh) exposures it generally will remain about two years without any great deterioration. In salt water, however, it will not stand a week, and when exposed to the sun and air, will be destroyed in about a month.

Each of the fossil resins represents a class that have many varieties, but none of them are coniferous. The latter class are those that furnish the turpentine and common resins of the present day, which are of the least value of any of the resins for a straight varnish or a pigment varnish. Their use in a varnish is principally on account of their cheapness and the slightly improved brightness they confer.

Records of the protective nature of some of these varnish paints show that a suitable combination of linseed-oil and a resin is a better protective vehicle than oil alone, yet the *smaller* the proportion of the common class of resins, the more *durable* was the coating.

In the oil and varnish trade, the essential differences in the quality of varnishes are due to the kinds of resin used, the proportion and quality of oil, and the care exercised in compounding them under the

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* Ures's Dictionary of Arts and Manufactures.

influence of a well-regulated long-heating process. The temperature and length of exposure to it necessarily varying with the different compositions and quality of the varnish required to meet the conditions to which it is to be subjected. Heats approximating the charring-point of the oil, 450°–500° F., are necessary for a thorough blending.

Varnishes and varnish paints dry better if moderately warm when applied, or if applied to a warm surface. Manufacturers of pianos and other highly finished surfaces on wood subject their work to 200° to 250° F. to aid the drying and to harden the coating.

But cheaper materials and processes than the above are employed to produce coatings to compete with the basic metal pigments for use on ferric bodies. This careless compounding has resulted in lowering both the price and quality of varnish paints, until many of the commercial varnishes fall below the average of the better class of straight pigment oil paints for protective coatings on ferric structures.

For trade convenience, 100 pounds of resin are taken for the unit of composition, and with this unit, 8, 10, 20, or any number of gallons of oil rated at 7.8 to 8 pounds per gallon, are compounded for the different grades of varnish, known as 8, 10, 12, etc., gallon varnishes. To designate the kind of resin used, the initial letter of the kind of resin that is employed is taken, viz.: An 8Z varnish means an 8-gallon Zanzibar; an 8M, an 8-gallon Manila, and so on, both for the single letters or with a combination of the letters.

In the color varnishes or so-called enamel or paint varnishes, where the pigments are ground in the selected brand of varnish employed for the vehicle, the designated letter of the resin in it is generally lost or withheld, except as specially furnished by the manufacturer.

All of these varnishes or paints are best thinned with turpentine to the proper consistency required for the brush. It is better for this purpose than oil. The heating of the oil and resin together for the varnish has so thoroughly incorporated them, that no free oil is present to exert any change or action in the drying process, separate from that present in the coating as a whole, and which the addition of free oil as a thinner would disturb.

Benzine, or other distilled hydrocarbon liquid, should never be used in the composition of varnish or varnish paint. Their quick evaporation results in making the coating porous, and liable to "check" or "alligator," as painters term it.

An essential point in either a straight or a pigment varnish is that the linseed-oil should be made from ripe seeds, cold pressed, and be well aged, and its "Mucossities" or non-drying elements (nearly 6 per cent of it) should be removed, in part at least, or so changed in character as not to be readily decomposed in the natural oxidation of the vehicle in the process of drying.

Dingles's Journal reports the experiments of Dr. Sace (Nuremberg) to ascertain the nature of different resins, viz.: Amber, copal, common resin, dammar, elemni, caramba wax, mastic, shellac, and sandarach. All of them were reducible to a powder form. Amber, elemni, mastic, shellac, and sandarach became pasty before melting, the others became liquid at once. Amber and dammar did not dissolve in alcohol. Copal became pasty, elemni and zaramba wax dissolved with difficulty, while common resin, mastic, shellac, and sandarach dissolved easily. Caustic soda dissolved shellac readily common resin partially, but had no influence on the other resins.

Oil of turpentine dissolved neither amber nor shellac; it swelled copal, dissolved caramba wax, common resin, dammar, elemni, and sandarach easily, and mastic very readily.

Boiling linseed-oil had no effect on amber, caramba wax, copal, elemni, or shellac, while sandarach dissolved slowly; common resin, dammar, and mastic dissolved easily in it.

Petroleum ether had no effect on amber, copal, and shellac, and was a poor solvent for caramba wax, common resin, elemni, and sandarach, and was a very good solvent for dammar and mastic.

Benzol dissolved common resin, dammar, and mastic very easily, elemni and sandarach to a limited extent, caramba wax more readily than elemni, but had no effect upon amber, copal, and shellac.

Though gums and resins are generally spoken of as belonging to the same class, they are distinguished from each other by the solubility of the gums in water and the insolubility of the resins in the same liquid. The gums are insoluble in alcohol, while the resins are soluble in it. The so-called gum-resins are soluble in both water and alcohol.

The *Trades Journal Review* (London), Dec. 4–14, 1901, p. 15, announces the discovery by Dr. Kronstein (Hamburg, Germany) of the "Synthetical Formation of Varnish Gums and Resins." These synthetical products are identical in physical and chemical properties with those occurring in nature. The discovery includes that of an intermediate product between the gums and resins, which invariably consists of twelve molecules, affiliating with "linoxin," the highest oxidation of linseed-oil. Dr. Kronstein produces an artificial resin identical with fossil amber, both in color and hardness; also has advanced his theory and process by producing the soft resins and balsams.

CHAPTER XI.

BAKED-JAPAN COATINGS.

For special locations and ferric constructions, viz.: riveted-steel water-pipe lines, anchor- and eye-bars, lattice-trusses, posts and beams, covering- or buckle-plates walled in or buried in masonry, and inaccessible for inspection, repairs, or repainting, a special coating called "baked japan" is being tested in a number of locations, the most prominent of which is a number of miles of steel water-pipe mains, 30 to 50 inches in diameter, riveted into a continuous length.

The process of manufacture and composition of the japan is similar to the black-varnish products, but a larger quantity of asphaltum, gilsonite, and other cheaper grades of gums and resins replaces the finer qualities of fossil and other resins. It is applied by immersing a *hot pipe* or other article in a hot bath of the compound, and upon removal from the bath and draining, baking it for a regulated period in an oven or muffle kept at an even temperature of 350° to 500° F., according to the size of the object to be coated, the composition of the japan, and the service required of the coating.

It fills all small interstices in the object, is elastic, will follow without strain all changes in temperature of the body coated, is perfectly impervious to atmospheric influences, running water, brine, acid, and alkaline and sulphur solutions, that affect the *ordinary* oil-paint coatings. Its cost per square yard of coated surface is naturally much greater than any brush coating, and will vary according to the conditions of its application. Its durability or life may be anywhere from ten to fifty times that of the ordinary oil-paint coating exposed to the same influences.

The composition of such baked coatings (and there are scores of them in practical use) appears to be of less importance than their proper proportion, and the care used in their combination, application, and final baking. It is reasonable, however, to expect that a compound that requires a high temperature to apply and to harden it will be durable, for the change induced by the heat in the final drying of the coating is not alone that due to evaporation, but is a thermochemical one, that may be supposed will strongly resist any influences tending to produce any other change than is subordinate to the original one that dried the coating.

Baked-japan coatings, from the nature of their ingredients, are electrically passive, except to currents of high potential; hence it remains for time to determine whether the stray electric currents, now a fruitful source of electrolysis in all ferric bodies that lie in the pathway of their return to their place of generation, will not find the rows of rivets that unite the several sections of the underground water-pipe lines coated with baked japan, the points to concentrate the electrolytic energy for a rapid corrosion of the pipe system at thousands of points in each mile, instead of a hundred or so, exposed in the usual spigot and bell method of joining the pipes. The electrolytic action at the rivets will be hastened by the difference in potential between the rivets and the pipe-metal—both of which are of different potential from the japan coating. The brush-paint coating applied to the rivet-heads will afford but little if any protection against corrosion or electrolytic action, as they will take place underneath the coating, and will require but a small development of either before they cast off the paint and have an easier field for their progress.

Another source of corrosion which these joints can resist but a short time is the action of the acid elements present in all earths. In the case of these water-pipe lines exposed for miles to a great number of strong electric currents, the ordinary rate of corrosion from earth and water will be intensified, as in the water-tower stand-pipe case cited in Chapter XXXIV of this volume.

While the baked-japan coating of itself leaves but little if any room for improvement in the coating of water-mains, it will surely be a source of future regret that a better method of joining the short sections of pipe into a continuous line was not adopted than the riveted joints thus far used.

If the brush or modified japan coating applied to the pipe circular seams is adequate for their permanent protection from corrosion, why incur the expense of a baked coating for the body part of the pipe? If it is not a permanent protection for them, then, as a chain is no stronger than its weakest link, there must be a great number of weak links in this method of constructing and protecting water-pipe mains that ought not to be repeated.

The interruption of the water-supply of a large city is too serious a matter to allow the question of a few hundred dollars a mile difference between a good and a bad plan of joint construction to be a factor in determining which to use. That a number of American cities have this bad joint is evidenced from trade catalogues and other illustrations of this method of constructing large water-supply pipelines.

The question has been raised as to whether the baking of the coating effects any further chemical union between the oil and the other constituents of the dip, other than that developed in the process of manufacture? It is probable that it does, as the baking temperature is materially higher than that in the process of manufacture. The pipe-coating material before baking is readily soluble in turpentine, but after baking is not softened by prolonged digestion in hot turpentine, and but indifferently in hot naphtha. The preliminary heating of the pipe before immersion in the hot-pipe dip assures its adhesion and impermeability, as the air and moisture are practically excluded and the preliminary bond of the coating to the metal is perfect. The evaporation of the volatiles in the japan dip in the process of baking is so quickly effected in the earlier stage of baking, that the liquid or fused mass of the resins readily replaces them and fills the interstices caused by their evaporation, and ensures a smooth unbroken surface to the coating altogether different from that of a dried paint.

The so-called japanned or enamelled coatings used on sewing-machines and many domestic machines and utensils are generally of that composition that will give the best appearance. They are not proof against corrosion under many exposures that would be resisted by a good varnish coating or an earthenware salt glaze. As a rule they chip easily, and corrosion once established in these spots, spreads rapidly beneath the enamel and flakes it off.

A properly made enamel is essentially a glaze, similar in composition and properties to glass, and has all of the advantages and disadvantages of that substance. It is melted at a high heat, 1200° to 1400° F., and adheres to the surface of metals perfectly. Enamels generally resist the action of acid solvents, but are brittle and easily chipped off.

"The best baked japans are intermediate between enamels and ordinary varnishes, and resist the action of solvents almost as well as an enamel, while they surpass the latter in the tenacity of the coating, allowing the metal they cover to be bent to a moderate degree without injury, while their elasticity is generally greater than a hard varnish. In hardness, baked japan is intermediate between varnish and glass, or harder than gypsum and nearly as hard as marble." *

Baked black japans are made from linseed-oil and asphalt as a base, mixed with more or less copal resins, usually kauri, and are thinned with turpentine. Like varnishes, the more linseed-oil they contain and the less driers (oxides of lead and manganese) the more durable they are; but to get them to bake hard at a comparatively low heat, the proportion of oil is frequently decreased as much as possible and the amount of driers increased, forming an inferior, brittle coating easily injured by a slight blow or rough handling.

Modern baked-japan water-pipe coatings are very similar in character and in their application to Dr. Angus Smith's anti-corrosive water-pipe coating, that forms the subject of the following chapter.

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* "Paints, Varnishes, and Enamels." A. H. Sabin, M.S., New York, 1896

CHAPTER XII.

DR. ANGUS SMITH'S ANTI-CORROSIVE WATER-PIPE AND OTHER COATINGS.

THIS compound was originally applied by Dr. Smith in 1840, and patented in England in 1850, and was first used in America in 1858 upon some pipes imported from Glasgow. Dr. Smith's original formula is not definitely known. Mr. James P. Kirkwood's Report on the Brooklyn Water Works, published in 1858, gave the following formula for it, and it was used to some extent upon the pipes for those works; evidently satisfactorily, for Mr. Peter Milne, engineer in charge of the extension of the works, reports: "That 36-inch pipe-mains laid for 35 years were found to be in perfect condition externally, and but few tubercules or other deposits were found on the inside of pipes." The pipes had been coated by heating them in an open furnace to about 500° F., and then immersing them in a bath formed from coal-tar, as follows: *

Coal-tar was distilled until the naphtha was removed and the material deodorized and of the consistency of melted wax or a thick molasses. This process also eliminated most of the tarry acids, and necessarily required considerable time and care to effect. Five to 6 per cent and in some cases 8 per cent of pure raw linseed-oil was then added and stirred in well. The bath was made deep enough to receive the pipes when placed in it vertically. The pipes remained in the bath until they had cooled down to the same temperature, about 300° F., or about 30 minutes for a 20-inch-diameter pipe. Careful attention was given to the length of time the pipes were to remain in the bath. A less time than 30 minutes for a 20-inch pipe gave an unsatisfactory result. For pipes from 4 to 12 inches in diameter, 15 to 20 minutes' immersion appeared to be sufficient to get a reliable coating.

When the coal-tar was distilled to the consistency of mineral

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* "Report in relation to Proposals made by various parties to protect the cast-iron water-pipes of the City of Brooklyn from corrosion." By James P. Kirkwood, Chief Engineer. City Document, published by Hosford & Co., 1858.

pitch or bitumen, or when common resin or Burgundy pitch was mixed with it and used as a bath, the pipe coatings became hard and brittle when cold, and the bath material would not answer, even where the quantity of linseed-oil used in it was increased to 15 or more per cent.

The preliminary heating of the pipes to 500° F. before immersion in the bath, after a short experience, was found to be prejudicial, and was abandoned. The combustion gases of the heating-furnace that were deposited on the pipes appeared to affect the bonding of the coating to the pipe-metal, and the pipes when removed from the bath were not satisfactory, and new specifications for coating them were adopted.

These specifications required the same preparation of the coal-tar for the bath as given above, and for it to be kept at a temperature of 300° F. during the period of dipping. As the material was continually deteriorating during the dipping process, fresh material was to be added frequently, and at least 8 per cent of linseed-oil, as near as could be guessed at, kept in the bath, or added with the fresh pitch. The bath was required to be occasionally entirely emptied of its contents and to be refilled with new material. The old material after a few days' use was found to be hard and brittle like common pitch.

Every pipe was immersed cold, but not frosty, and was to remain in the bath until it had attained the temperature of the bath, 300° F. This period was about 30 minutes for the 20-inch pipe, as in the previous specification. It required a brisk fire to be maintained under the bath to overcome the cooling action of the cold pipe when immersed.

The presence on the pipe of moulding-sand, dirt, moisture, frost, or oil and grease of any kind, was found to be detrimental to the application of the coating, and their removal was necessary before dipping.

The royalty paid Dr. Smith for the use of his formula, although no United States patent was in effect, was 37½ cents per ton of pipe.

The price paid the English pipe-founders for coating the pipes ordered from them by the Brooklyn Water Works was $1.25 per ton, for the years 1858 to 1860. American pipe-founders' and contractors' price for Dr. Smith's coating was about $3.00 per ton as against a plain asphalt coating of $1.83 to $2.25 per ton.

The efforts of other water-works' engineers to follow Dr. Smith's formula, and possibly to improve or cheapen its application, resulted in so great a variety of recipes and consequently inferior results, that but little dependence can be placed upon their reports. The temperature of the preliminary heating of the pipe before immersion varied from 200° to 700° F., and the proportion of ingredients and their composition was equally startling, as were also the attending results.

Mr. Chas. Harmony, Chief Engineer of the Louisville, Ky., Water Works, who experimented for a number of years with Dr. Smith's formula as given by Mr. Kirkwood, reports: That "*some* of the pipes so coated, after an exposure of from six to eighteen years, were in as perfect condition as when first laid; but it was an exception, not a rule. In a majority of cases the coating on the inside of the pipe was all gone, and upon the outside surfaces it had apparently been of no importance in prolonging the life of the pipe. The difficulty experienced was, that in the heating of the bath to the temperature of 300° F., the coal-tar, resin, and pitch compounds became unmanageable by approximating the condition of boiling and volatilization, and going everywhere except in the place it was wanted. The coating was thick and apparently unbroken, but exceedingly brittle, and would crack and scale off in the ordinary process of handling."

The tension of coal-tar and pitch at a temperature of 300° F. is hardly less than that of water at the same heat, or equal to about 53 pounds' pressure. To maintain such a temperature in the bath in open atmospheric pressure is impractical, and the composition becomes unmanageable.

Other engineers report that the pipes after twenty years of exposure were found to be free from corrosion, but the coating had lost its bond to the pipe, and evidently remained in place because corrosion or other causes had not developed enough energy to cast it off against the pressure of the surrounding earth.

In these and similar instances of failure, the results appear to have been more markedly against pipes cast in greensand instead of a dry sand or loam-mould, evidently because the thick, vitreous, or partly fused greensand coating carried so much air in its rough, sandy surface into the bath, that it could not escape through the heavy pitch composition. Furthermore, this varnish itself was overcharged with its own vapors under tension, and of greater density than the air, and confined them until the cooling of the pipe when removed from the bath rendered their escape impossible, hence the irregularity in the results. Had the pipes been baked in an oven after removal from the bath, as in some recent applications of this compound, the rough, vitreous sand coating on the pipes doubtless would have ensured a more enduring coating than the same compound applied to a smooth, dry-sand moulded surface, or one of rolled wrought iron or steel. This silicate coating would be reinforced by the tough Bower-Barff skin, to which it is naturally so closely attached as to require pickling to remove. It is the subsequent baking that the pipe receives that renders this process a success. The composition of the bath can be varied greatly without much detriment to the protective nature of the coating, if the baking process follows the bath.

The generally unfavorable results attendant on the use of Dr. Smith's formula without the baking process, and the care and cost of it, determined the present practice of the pipe-founders, which is to place the pipes for a short time in an oven heated to 250° to 300° F., then immerse them in the bath of hot coal-tar and pitch, and then cool them in the open air.

This coating is one of appearance more than of a protective or an enduring nature, and is only applicable to water-pipes, as in gas-pipes so treated the solvent action of the hydrocarbon vapor soon removes the coating, and the joints draw and leak worse than with the uncoated surfaces.

The careless and indifferent boiling of coal-tar, to free it from its many acid and other impurities, makes it a variable and unsatisfactory coating. Lime, gypsum, and other mineral substances mixed and boiled with the coal-tar to neutralize the ammonia, acids, sulphur, etc., only render the tar more unreliable and unmanageable. The careless heating of the pipes and bath, also the length of time the pipes are left in the bath, and the subsequent treatment of the pipes when removed, are all factors in the indifferent results obtained.

Unless great care is exercised the small pipes will be overheated and unequally coated and brushed off, inside and outside. The larger pipes, requiring a longer time to heat, from the mass of metal they contain, will be underheated in the oven and cool down the bath to a lower degree than is requisite for a reliable coating. The subsequent brushing of the coating, both inside and outside, during the first period of cooling (a matter of from 30 minutes to 2 hours), promotes its reliability.

All coal-tars or their compounds of whatever nature used as a bath, or applied with a brush to any surface, hot or cold, are subject to the law of fractional distillation; that is, that such a mixture during the process of distillation remains at the boiling-point of that constituent which boils at the lowest temperature until that constituent is exhausted, then changes to the next boiling-point, and remains there for a time, and so on.

The low boiling- or evaporating-point of the lighter elements of coal-tar or petroleum products makes them very uncertain in their composition, as changes of temperature in the bath from 220° to 350° F. are frequently noted without any change in the character of them that the eye can detect.

The character of the bath composition changes so continuously and rapidly during the dip that frequent additions of fresh stock must be made. These necessarily cool the bath, change its composition, and irregular coatings ensue to that extent that an entirely new bath is necessary.

The use of linseed-oil with coal-tar for pipe coatings, as usually applied at the pipe-foundries, is of very uncertain value. It causes the dip compound to froth to nearly double its volume, and renders the coating lumpy in appearance and uncertain in its bond to the pipe-metal. It requires some effort by continual stirring to incorporate it with the coal-tar and pitch, and it is always liable to separate from them and float upon the surface, froth, soften the coating, and delay its drying.

Dr. Angus Smith evidently used a number of formulæ for pipe coatings that contained linseed-oil as one of the ingredients. A long line of careful experiments with the best of coal-tar, pitch, and linseed-oil carefully heated and applied, gave almost uniformly good coatings. Using the commercial grades of these substances and having the ordinary day laborer to compound and apply them, the result was necessarily inferior, so much so as to cause the abandonment of linseed-oil in coal-tar pipe coatings by modern founders. If, however, the truth were acknowledged, the present coal-tar pipe coating would be found to be living on the well-earned and deserved reputation of Dr. Smith's compound.

Dead Oil in Pipe Coatings.

That part of coal-tar obtained in the fractional distillation of the tar between the temperatures of 410° to 750° F., and which contains creosote and anthracine oils (see Analysis, Chapter IX), is used to keep the pipe dip at a standard quality. It evaporates by itself, about one-seventh as rapidly as water, when both are at atmospheric temperature.

One part of dead oil to about seven parts of coal-tar increases the proportion of the heavy oils in the tar dip from about 25 to 35 per cent, and appears to make the coatings more uniform and of a better character than where *fresh tar* is used to reinforce the bath.

Thick tar gives thicker and more uniform coatings than thin tar, and fresh tar requires a hotter pipe to take bond than does old tar.

Crude gas coal-tar boiled from five to six hours becomes a soft solid at atmospheric temperatures. During the boiling the temperature remains at about 220° F. for about an hour, then rises to about 290°, stays there for a time, and finally rises to about 350° F. All of the naphtha is removed and the tar is deodorized and reduced to the consistency of very thick molasses. If to sixteen parts of this tar 1 per cent of boiled linseed-oil be added, no frothing occurs even at 400° F. The mixture is thick and does not harden well on light iron pipes about ½-inch thick. On heavy iron pipes an inch or more thick, the coating hardens without difficulty; in some cases becomes too hard, is brittle, and flakes off readily by mechanical injury when handled. Dead oil added to thin the mixture causes no frothing. The experiments show that linseed-oil could be used with success and advantage with partially refined coal-gas tar, and also indicates that its application requires more intelligent care than the methods employed with the usual crude tar coating.

Experiments with a refined tar containing dead oil show that as high as 8 per cent of boiled linseed-oil resulted favorably in solidity and hardness of the coating. In other instances, where from 1 to 8 per cent of raw linseed-oil was used instead of boiled oil, frothing occurred and a poor coating resulted, evidently due to the presence and evaporation of the water in the raw oil. There is about 5 per cent of water naturally held in combination with the best quality of raw linseed-oil made from ripe flaxseed, and nearly 8 per cent in the oil made from unripe seed. With many brands of commercial linseed-oil, 10 per cent additional of water is frequently incorporated by stirring it in with a paddle or passing it through a mixing mill. All such oils are likely to be made up from fish, resin, mineral or vegetable and animal oils with no linseed-oil of any quality in them, and all the difficulties developed by these mixtures with the coal-tar are saddled upon the scapegoat, linseed-oil.

Refined coal-gas tar is practically out of the market and has been for many years. What small amount of crude coal-tar is available is too valuable and in too great demand for the chemical products in it to allow of its use to the great extent that pipe-founders require for their work. Heavy roofing pitch alone will run in moderately warm weather and becomes too soft and sticky for a pipe covering, unless laid immediately after coating. This is impracticable, and in cold weather it is too hard and brittle for transportation or handling.

Nine parts of heavy roofing pitch with one part of boiled linseed-oil give a thick glossy coating less brittle than pitch alone.

Two parts of boiled linseed-oil with the nine parts of the pitch give a coating more elastic and tough.

Three parts of boiled linseed-oil with nine parts of pitch, the coating is more bulky and less smooth than with the others, while with larger proportions of the linseed-oil the coating partakes of the character of a slow-drying paint and requires baking, which gives it a superior quality.

Coal-gas tar belonging to the class of pyrogenic (fire-formed) compounds is unstable at ordinary temperatures, and is continuously decomposing by the evaporation of its many hydrocarbon elements, until nothing but the hard friable pitch is left, which contains nearly all of the sulphur element in the coal that forms the base of the tar product. Asphaltum, also a pyrogenic product, formed by the slow evaporation or distillation of petroleum, decomposes upon exposure by reason of the oxidation of the sulphur element in it, but is more durable than the coal-tar residuum or pitch (asphalt).

Asphaltum and linseed-oil coatings do not harden well, unless a hard grade of asphaltum is used.

Water-pipe Dips and Coatings.

There are many pipe dips upon the market, some covered by patents of doubtful validity, others secret or proprietary compounds of doubtful utility. Some of these compounds appear as pipe dips, also as brush paints applicable for ferric constructions other than pipes. (See Paint Tests, Chapter XXIX.)

The P. and B. Pipe Dip is a patent dip; the principal ingredients are probably an asphalt and *candle-tar pitch.* The latter is a pitch obtained by the distillation of animal fats or refuse. Upon pipes its coating is similar to an asphalt coating, not hard nor brittle, not very glossy nor very tenacious.

The P. and B. Universal Paint is an asphaltum paint; the vehicle contains carbon disulphide as the volatile element, the evaporation of which is not only nauseating and dangerous to all animal life, but carries the danger of explosion and fire risk. Whatever good qualities it may possess when on, are more than offset by the dangers connected with its application.

The P. and B. "Ruberine" consists of "ruberoid" dissolved in naphtha. "Ruberoid" consists of California asphaltum or maltha and candle-tar pitch digested and vulcanized with sulphur. "Ruberine" dries rapidly, is hard to spread smoothly, but gives an elastic or rubbery coating. See tests of paints, New York Elevated Railway Viaduct, for an example of its qualities.

Mineral Rubber Dip (or Rubber Coating) is a secret composition whose appearance indicates that it is largely asphaltum. It is rather duller in appearance than the ordinary coal-tar or asphalt mixture. The dip requires a temperature of about 400° F. to apply, and then it is almost impossible to get a smooth or neat-appearing surface. As yet its protecting qualities have not been determined.

"Bitumastic" Products comprise an enamel to be applied in a molten state to the metal. Bitumastic cement is used hot for the preservation of ships' bilges and frames, instead of the usual hydraulic cement coatings, and also for the protection of water-pipes. *Bitumastic solution* has bitumen for its base. It is a brilliant black paint applied the same as other paints, and is probably similar in character and composition to "Smith's Durable Coating." It has been used to a considerable extent on steel water-pipes and for the limited period of test in that service is favorably spoken of. It dries in 24 hours, is said to be unaffected by acidulous, alkaline, or brine solutions. If applied to the clean dry surface of the metal, does not crack or peel when alternately wet or dry, or exposed continually to running water in penstocks, water-wheels, etc. It is not affected by a moderate heat, nor by sulphur fumes, and is furnished ready for use at $1.75 per gallon. It is very volatile, and the packages must be well stirred while being used. Its covering power is about 400 square feet, and its weight about 9.5 pounds per gallon.

"Crysolite" Enamel and Paint. "Crysolite" paint is made from oil and a by-product, oven-coke. It weighs 9.5 pounds per gallon and spreads 500 square feet as furnished for a paint. When thinned with 12.5 per cent of oil, will cover 1000 square feet, and under general conditions in both hot and cold weather, dries completely in 30 hours. *"Crysolite" Enamel* is a quick-drying paint of the same character as the above, and dries in one hour. "Crysolite" products are alkaline in reaction, whereas coal-tar products in general have an acid reac-

tion. "Crysolite" is better for being applied warm or hot (as all ferric paints are). In the winter one-eighth of its volume of turpentine can be added to aid its spreading power, which can be made to cover from 800 to 1000 square feet. "Crysolite" paints cost about 75 cents per gallon mixed ready for summer use.

"Crysolite" coatings on ammonia tank-cars and reservoirs stand the action of ammonia liquors and gases better than most of the paints used for this purpose. "Crysolite" baked coatings under test resisted the action of carbonate of ammonia and ammonium chloride liquors for three months without injury. "Crysolite" under the influences of strong brine is more favorable than the commercial asphaltum or the ordinary coal-tar paints.

Hickenlooper's gas-pipe-dip compound, used by the Cincinnati Gas Light and Coke Company, the United Gas and Improvement Company, and several other gas companies, to coat their small service pipes, has a record of many years' exposure in the ground with few traces of corrosion. The failures thus far reported show that neither the process nor compound were at fault, but the lack of thoroughness and intelligence in its application. The pipes are first cleaned from rust and mill-scale and then immersed in the following dip and in the following manner. Twenty gallons of retort coal-gas tar are brought up to a boiling heat for a short time to evaporate as much of the water, acids, ammonia, etc., as possible, then 20 pounds of freshly slaked lime are sifted in from the top and well worked into the tar. Boil down to the consistency between a coal-tar and a pitch. When settled, add four pounds of tallow and one pound of powdered resin; stir until all are dissolved and thoroughly incorporated, then let the mass cool and settle; then ladle off into barrels. When ready for use, to each barrel of forty-five gallons of the above mixture add four pounds of crude india-rubber dissolved in turpentine to the consistency of thick cream. Heat the mixture to about 150° F. and immerse the pipe, *previously heated* to about the same temperature. After a few minutes' immersion the pipes are removed from the bath and laid upon skids to harden. The coating is somewhat softer than the usual pipe-founders' dip, and requires more time to harden, and continues hardening for a number of hours after cooling down to atmospheric conditions. The compound is especially useful in coating the screwed ends of threaded pipes. It is better for this purpose than the red-lead compounds usually employed.

All rough coatings are detrimental to the life of water-pipes.

Upon the inside surfaces the pits or cavities that constitute the rough surface of the coating are the first to catch the saline, sulphur, or other impurities in the water that form the basis for the development of the rust cones. The coating under these pits is the first to break down, being of inadequate thickness—probably only $\frac{1}{500}$ inch thick. The external surface of the pipe is as rough as the inside, and is not only exposed to the moisture to inaugurate corrosion, but this moisture will contain all the acids in the soil in which the pipes are laid.

In all cases of the corrosion of water-pipes, it is the porosity of the coating that causes the formation of the tubercles and decay of the pipe. Nearly all of the dip coatings, when tested by themselves or not in contact with ferric substances, were practically uninjured by acid solutions or running water.

In general, all pipe coatings, applied as they nearly always are in a careless, indifferent manner, will begin to show indications of tubercles in three years, and cases of tubercles in large pipes at the end of sixteen years have been noted, where the carrying capacity of the pipes had been reduced 20 per cent.* Engineers must earnestly take up this question of reduced carrying capacity of their water-pipes and decide whether it is not more economical to add from 5 to 10 per cent to the cost of the pipe in the form of better coating materials and better methods of their application than to submit to this decrease in flow, that always grows less with the age of the pipe, while the demand upon the service is always increasing.

Specifications for pipe coatings appear to be of little use in producing a satisfactory coating, either in appearance or durability, as the directions they give are more often evaded than carried out by the foundry employés. After the pipes are coated and upon the drying skid, no ordinary inspection can determine the character of the coating other than its appearance to the eye or touch.

Testing pipe coatings is usually by the hammer to see whether the coating is so hard and brittle as to chip off in handling. The acid test determines the porosity of the coating by attacking the metal through the pores of the dip. A solution of one part muriatic acid and two parts water will affect both the coating and the covered metal more at the end of sixty days than they would be affected by ten years' exposure to running water. In nearly all cases where the

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* Excerpts from a paper by Desmond Fitzgerald, C.E. Transactions American Society Civil Engineers, Vol. XXXV, 1896, p. 241.

coating has been dried by heat or baked, the metal will be corroded $\frac{1}{16}$ inch or more, the coating undermined and peeled off.

After all, in this age of specifications, inspections, scrimping, and adulterations, there is nothing equal to an honest and capable contractor, either for furnishing pipe, coating, inspecting, or laying it. Get such a one if possible and then watch him closely.

Generally, the time that the pipes are left in the hot bath does not exceed one minute, and is more often only one-half a minute. It is impossible to properly coat a pipe in one-half a minute, as the air carried into the thick turgid bath by the pipe will not escape in that time, and the top part of the inside of the pipe and the lower part of the outside of the pipe are uncertainly coated for this reason. The pipes are seldom turned over while in the bath, or outside while on the skids in the process of scraping and brushing off the surplus dip.

On pipes that are left in the bath for five minutes the coatings are markedly superior to those exposed for shorter periods. This is the case whatever the nature of the coating, and is one reason why the Angus Smith and other older-day coatings gave such superior results to those coated by modern methods. They never had less than five minutes in the bath, and were often left for fifteen or even more in case of large pipes one inch or more in thickness. Modern pipe-foundry management allows no such exposures.

A coal-gas tar paint that has given very good results in the coating of gas-holder tanks and other situations where the metal is exposed to ammonia and sulphurous acids in solution and to alternate melting and drying under a great range of temperature, is made as follows: Coal-gas tar is well boiled to evaporate the water and light hydrocarbon elements and then 20 to 25 per cent of caustic quicklime is sifted and well stirred in to neutralize the acid elements in the tar. This is to be kept hot for a few hours and then an equal quantity of good Portland or hydraulic cement is sifted and stirred in thoroughly. The mixture is applied hot to the clean dry iron, and can be repeated soon as cool or dry if the exposure conditions are to be very severe. In the latter case, a little more cement should be added, so that the caustic lime and cement mixture will contain 50 per cent of each. The pigments thicken the coal-tar and prevent it from running under sun temperatures and give a bond to the brush coating of neat Portland cement that should be applied to the coal-tar coat as soon as either the first or second coat of the mixture is dry. This coating can be repeatedly applied with advantage. It is impervious to gases and water and has no tendency to run at temperatures under 130° to 140° F.

Mr. Born, in "Comptes Rendes," in 1837, called attention to the fact that iron cast in charcoal-coated or chilled-iron moulds was less susceptible to corrosion than greensand castings.

The city of Perth, Scotland, where very pure water is obtained from the Tay, had their water-pipes coated with a solution of india-rubber. After 25 years of use every pipe under 5 inches in diameter had been completely closed by corrosion. In many cases where the ordinary coal-tar dip had been used on the water-pipes it scaled off in strips and was discharged at the house service-taps.

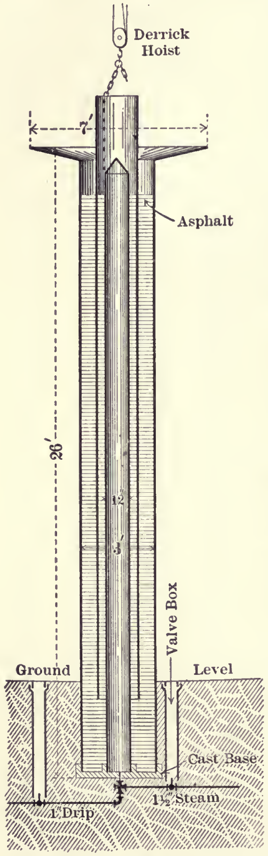

Fig. 21.—A pipe-dipping tank.

A pipe-dipping tank being required for some steel riveted pipes, 16 to 30 inches in diameter and 28 feet long, was extemporized from old material in the contractor's yard, and is shown by the following Fig. 21.*

An old boiler-shell 3 feet or more in diameter and 26 feet long was fitted with a slightly dished wrought-iron flange 2 feet or more in width all around, riveted to the top end of the shell. This served as a working platform, also to catch and return the drip. The other end or lower one of the shell was riveted and caulked to a cast-iron plate-head which carried on its inside face a concentric flange in the centre, to which was riveted steam-tight a wrought-iron pipe nearly as long as the outer boiler-shell. This inside pipe was closed steam-tight by a conical head that also served as guide for the pipe when it entered the bath of pipe dip. The bottom flange was tapped for steam- and drain-pipe connections, which were fitted with the usual gates, worked from the surface of the ground, in or on which the tank was erected. The annular space between the centre pipe and shell was filled with the coal-tar or other pipe dip to be applied to the pipe, which was kept hot by the steam

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* *Engineering Record*, Vol. XXXV, May 8, 1897, p. 489.

in the centre pipe. The immersion and withdrawal of the pipe to be coated kept the bath mixture well stirred up and ensured a nearly uniform quality of its ingredients. It is obvious that this comparatively inexpensive device is adaptable for many occasions that would not warrant a more expensive plant.

A larger shell could be fitted with a number of the conical-headed pipes with their separate steam- and drain-pipe connections and be available for dipping a number of pipes at the same time, and would certainly ensure a more reliable coating than where the pipes are immersed in a long horizontal tank.

Approximate Relative Cost of Various Pipe-Dips and Coatings.*

Coating.	Approximate Amount Required to Coat One 48-inch Pipe, 12 Ft. Long.	Approximate Prices.	Cost of Material for One 48-inch Pipe. Approximately 325 Sq. Ft. of Surface.
Crude tar	3¾ gals.	$3.00 per bbl. (52 gals.)	$0.22 *a*
Pitch	5 "	5.00 " " " "	0.50
Pitch and linseed-oil	....	....	.70
P. & B. dip	20 lbs.	45.00 per ton	.45
Mineral dip	20 "	75.00 " "	.75
P. & B. universal paint	1½ gals.	1.00 per gal.	1.50 *b*
P. & B. ruberine	1½ "	1.00 " "	1.50 *b*
Tar varnish	1½ "	0.10 " "	.15 *b*
Dutch varnish	1½ "	0.25 " "	.40 *b*
Sabin's baked japan	1½ "	1.75 " "	2.60 *c*

a. About 30 per cent of this was lost by evaporation.

b. Estimated cost of this coating as applied with a brush. The wastage would be excessive as a dip, but the dip is the only practical way for its use on a large scale, hence the figures are not strictly correct.

c. This coating requires a comparatively expensive plant and considerable skilled labor, which would largely increase the total cost.

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* "The Manufacture and Inspection of Cast-iron Pipes." Thos. H. Wiggins, C.E., Boston. *Civil Engineers' Association Journal,* 1899.

CHAPTER XIII.

GRAPHITE AND GRAPHITE PAINTS.

CARBON assumes in nature three allotropic forms, viz.: Diamond, graphite, and amorphous carbon. Graphite itself assumes different forms, some of which are amorphous and others strictly crystalline in character.

If the three allotropic forms of carbon had each a characteristic name, no confusion would be liable to arise in speaking of them. We speak of the diamond and of graphite, and each is clearly defined.

In speaking of the third form we are limited to amorphous carbon. This form is found in certain stages which are not strictly amorphous or granular in character. Coke, for instance, is one form; the others are the mineral graphite-carbon or graphite, termed foliated (flake), amorphous (granular), etc. Graphite is found in many parts of the world and is of various degrees of purity, ranging from 60 to over 90 per cent of graphitic carbon in the foliated form and 20 to 60 per cent in the other forms.

The foliated is a designation for the thicker flakes in the Ceylon and like varieties, while flake is used to designate the thin flakes of the purest brands, similar to the Ticonderoga mine product.

The German (Bavarian), Siberian, Mexican, and some American varieties are amorphous and vary greatly in the amount of carbon in their composition, as will be seen from the following analyses:

The purest brands (Ticonderoga mine) have a specific gravity of 1.21 to 1.4. The amorphous varieties range from 1.80 to 2.25 to 2.79. When pure it is perfectly opaque, iron-black or steel-gray in color, with a metallic lustre. Its hardness varies from 1 to 2, and it conducts electricity nearly as well as the metals.

Pure graphite or minerals high in graphite-carbon grind and feel greasy, and are repellent to moisture and oil. Flake-graphite above 80 per cent in purity, by long trituration with water, can be reduced to a fine lamina or pigment.

Anthracite coal is an intermediary carbon between graphite and bituminous coal. It is blacker than graphite, hardness 2 to 2.1 as against 1 to 2 for graphite when it contains 95 to 99 per cent of carbon.

The Ceylon, Cumberland, Indian, and American flake varieties are the purest in carbon, and are used for pencils, crucibles, lubricants, stove-polish, foundry facings, etc., and to tone up the poorer varieties for many purposes.

Foliated graphites, though used for pigments, are not as satisfactory (for reasons given hereafter) as the amorphous variety, that, less rich in carbon, contains other mineral substances, non-corrosive, non-absorbent of atmospheric moisture and gases, either as individual substances or collectively as a natural mineral compound. That this feature may be duly considered when a graphite pigment is to be selected for a ferric structure the following analyses of amorphous graphite from a number of widely separated mines are given:

ANALYSES OF AMORPHOUS GRAPHITE.

	Siberian and German Mines. Per Cent.	Lake Superior U. S. A. Mines. Per Cent.
Graphitic carbon	33.20 to 36.06	28.39 to 33.48
Silica as SiO_2	43.20 " 37.70	46.97 " 37.54
Iron soluble as Fe_2O_3	3.05 " 4.02	4.22 " 4.25
" insoluble		
Alumina as Al_2O_4	15.42 " 17.80	16.90 " 12.35
Calcium as CaO	1.06 " 1.20	0.99 " 1.02
Magnesia as MgO		
Carbon dioxide, water combined, sodium compounds, iron pyrites, volatile matter and loss	4.09 " 3.22	2.53 " 1.36

Specific gravities, 2.25 to 2.79. Color, gray or drab. Hardness, 1.5 to 1.8. Fracture, granular.

Graphite from the Wisconsin mines analyzes, viz.:

Graphitic carbon	72.00 to 74.00 per cent
Iron oxide	7.10 " 14.00 " "
Silica	10.00 " 12.00 " "
Alumina	8.00 " traces
Water and undetermined	2.90 " "

The Mexican graphites are amorphous in character, are high in carbon, and have had but a limited use for pigments. When containing about 80 per cent of carbon they are better suited for lubricants or foundry facings.

The amorphous brands of graphite require no calcination other than necessary to dispel the water, natural to all minerals, preparatory to any pulverizing operations. They grind fine and granular, and in an approximately cubical form, are not repellent to the oil or vehicle, and are nearly as unoxidizable from moisture, atmospheric influences, combustion, and other gases as pure carbon. They are of an agreeable color and good covering power, and they work well in combination with other pigments; flow, hold, or carry well in the oil, and are as easily brushed out to cover as much surface as any good paint. They are not repellent to the oil, do not separate from it, nor set in the paint pot or barrel on long storage, either as a paste or paint. They are wholly self-supporting as pigments, contain no elemental substances that tend to reduce them to a lower plane by oxidation or slacking in the presence of moisture and gases. They require no body stuffing, either to bond them, or to keep them quiet, or from curdling or crawling during or after application, and they contain neither acids nor sulphur.

They are entirely different in character and composition from the so-called silica graphites of commerce, many of which resemble carbonaceous schists or impure soapstone, or are compounded from flake-graphite and mineral substances of dissimilar character, such as barytes, silica, furnace slag, etc. These several substances, even if they are non-corrosive, or electrically or chemically passive of themselves or collectively, when assembled in a paint cannot be as reliable as are the same substances incorporated together by the processes of nature, each and every particle of which is of the same physical and chemical composition and equally affected by the vehicle, atmosphere, or other conditions that affect a paint.

They have not the merit of being synthetical compounds. No human care in the mechanical processes of grinding and mixing them, as a compound pigment or paint, can arrange them in sequence or in other than a haphazard manner.

Silica graphite paint is of a dark, lifeless brown; not objectionable on the enclosed ironwork of a building, but decidedly so for more prominent positions. Hence it is toned up by red lead or other basic pigments of agreeable color, but at an increased cost and a contributed element of danger in the disintegrating of the paint whenever hydric-sulphide fumes reach the red lead in the coating.

Iron oxide is also used for toning effects, but the natural red hematite oxides are not strong enough in color to materially modify the dark brown of the graphite, silica, and barytes compound, unless excessive quantities are used, which bring into the coating all of the uncertain elements of that class of pigments that thus far have proven to be the most unreliable of all ferric coatings. The danger is greater if the brighter red copperas oxides are used. Their strong sulphur element sets into action an antagonism between every element in the coating and delays the drying of the paint, making necessary excessive amounts of strong driers to counteract even a small percentage of it.

Graphite paints are noted for being slow driers and require a liberal use of driers to get a firm coating. This is more apparent with flake-graphite; its flocculent form and oily nature prevent the vehicle from bonding it. There is a movement in the paint during the whole process and period of drying that even the sharper and more angular form of the silica or barytes added cannot wholly overcome. Furthermore, these substances bring their own peculiarities into the coating and forcibly demonstrate the unreliable character of all compound paints. The greater the number of substances in a paint the less dependence can be placed upon them to work together for a durable coating. An acid and an alkali will chemically form an innoxious whole, but this or similar action is dangerous in a drying paint and generally proves detrimental to the coating or covered surface.

High-carbon graphite is so easily adulterated with soapstone that if a pound of it be ground with three pounds of soapstone (specific gravity 2.7), neither the eye nor touch can detect the adulteration; only analysis will show it.

Graphite is one of the lightest pigments. Its specific gravity ranges from 1.21 to 1.4 to 2.38, while zinc oxide is 5.42, asphaltum 1.4 to 1.8, barytes 4.5 to 4.7, silica 1.9 to 2.8, gypsum 2.15 to 2.35, iron oxide 4.7 to 5.4, whiting 2.2 to 2.8, red lead 9.07, white lead 6.43.

The natural drying of a linseed or varnish coating is in the form of a closely woven web of a fine fabric. This shows plainly on a freshly dried or drying surface, and explains the reason why two or more coats are necessary to give a smooth foundation for the last or polishing coat. Each subsequent coat fills the interstices of that underneath it, each coat repairing the other's deficiencies, as many folds of a fine muslin will in the aggregate make an adequate covering from heat or light.

Now, it is the function of a pigment to fill these cellular formations in the drying vehicle, or rather, while being applied with a brush, for the atoms of the pigment, mechanically arranged in brushing out the paint, to lie side by side, all embedded in the vehicle, which in drying naturally takes the lines of least resistance, i.e., between the pigment atoms, and, as it were, each atom lies in an approximately square hole, the most favorable condition for the bond between the pigment and the vehicle.

If the pigment atom be splintered like a sliver of glass, or of only length and breadth like a flake, then the natural cellular formations in the drying vehicle cannot be realized. Such shaped pigments are arranged with the sharpest angles and edges upright to the drying surface, and are not well covered in or embedded in the oil, hence dry with a rough surface that will hold moisture and dust and quickly decompose and disintegrate them from their bed, when more moisture, cinders, and dust take their place and the cycle of action is repeated.

The rough character of all paint coatings containing silica, barytes, furnace slag, etc., is distinctly apparent to the touch. A round marble does not bed itself in a cement as well as the cubical block from which it is made, neither does a beach-worn sand or a quicksand atom, with the best of cement, make a good mortar for the same reason. The splinters, flakes, and round atoms are more easily removed from their beds than a square atom.

Both the amorphous and flake graphite pigments (not associated with foreign substances as adulterants) being electro-negative, are less affected by catalytic or electrolytic action caused by the juxtaposition of electro-positive substances in the coating or surface covered, or by hydro-sulphide gases, than any class of pigments, lampblack alone excepted. This is a valuable feature in any paint, whether applied to iron or wooden bodies, and in the future will insure a more extended use of graphite paints instead of the iron oxides, and compounded or patent paints, to the careless use of which most of the corrosion in progress upon important ferric structures is directly traceable.

As a general rule graphite minerals that contain about 40 per cent of graphitic carbon have proven to be better for pigments than those richer in carbon, for the reasons given before, the principal one being that they are less repellent to the oil and bond better to it, and do not appear to be affected by combustion gases.

Amorphous graphite coating applied to boiler tubes exposed to internal firing and the action of hot water under pressure of eighty or more pounds per square inch for two years was uninjured and fresh as when it was first applied.

Fig. 22 shows a boiler-tube thus exposed. The tubes had been in the boiler for a number of years, when they were removed and cleaned from the hard silicious scale that covered them. When they were replaced, each alternate tube was coated with Lake Superior graphite paint, the others being uncoated. At the end of over two years a number of the tubes were removed and their condition ascertained. The unpainted ones were again covered with the hard, flinty scale, that required the use of a boiler-scraper to remove. The painted tubes were covered with a light flocculent coating of the scale, that could be brushed off with the fingers, showing the bright, clean paint beneath it. The tubes were pitted with rust in spots and streaks when they were first removed to be cleaned. These show in the photograph, but the corrosion was stopped by the paint. The light-colored scale-deposit was left on part of the tube, and shows on the sides of the figure.

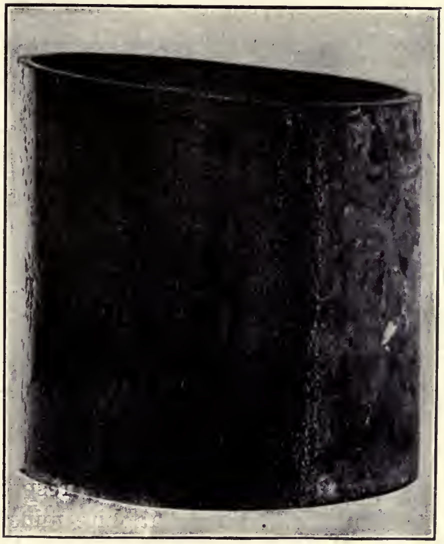

Fig. 22.—Boiler-tube.

Pieces of iron coated with graphite paint and dipped in muriatic, sulphuric, and nitric acids, and allowed to dry with the acid on them showed at the end of nineteen days no injury to the coatings. Other samples immersed in alkaline and other chemical solutions, also in coal-oil for a number of weeks, and strong brine for months, showed but little injury. Other tests of endurance of all brands of graphite paints showed a marked superiority over other basic pigments, whether prepared for a test or compared with the commercial brands of other paints.

While tests of paints are not regarded by many engineers as indicative of their value to resist the ordinary influences upon a coating exposed to weather, they do show that a coating that can withstand the above severe tests is certain to give more satisfactory results in its general use than the many commercial paints whose low price and not their protective qualities is their principal recommendation. They also show that if the conditions to which a coating is to be subjected are known, it can generally be furnished to successfully meet them.

Other tests of graphite paints in competition with other commercial paints are given in the following chapters on paint tests. For a roofing paint the graphites high in carbon, of themselves, or mixed as silica-graphite compound paints, are of marked excellence. They do not harden as rigidly as the iron oxides used for roofing purposes. They endure long exposure to the sun, hence are less liable to crack or flake off, and they follow without injury the expansion changes in the metal they cover. Their darker color and higher cost compared with iron-oxide paints used for roof coatings are more than offset by their better protective qualities and longer life.

Electric-furnace Graphite.

However engineers may differ about the respective merits of a low or medium grade of amorphous-graphite mineral for a straight paint compared with a flake-graphite and silica compound, their attention is liable to be attracted in the future to a new product that has entered the field for a pigment, under the name of

"Acheson Graphite."

This substance is an amorphous-graphite pigment of high-carbon content, whose physical character seems to be materially different from the high-carbon mineral graphites heretofore used for paints. Although amorphous or granular in character, as compared with the other forms of graphite, such as the flake-graphites, it is nevertheless distinctly a graphite product, and contains absolutely no trace of amorphous carbon, the name usually applied to such forms of carbon as lampblack, coke, coal, etc. Graphite in any form is much more inert chemically than these amorphous carbons, but Acheson graphite is

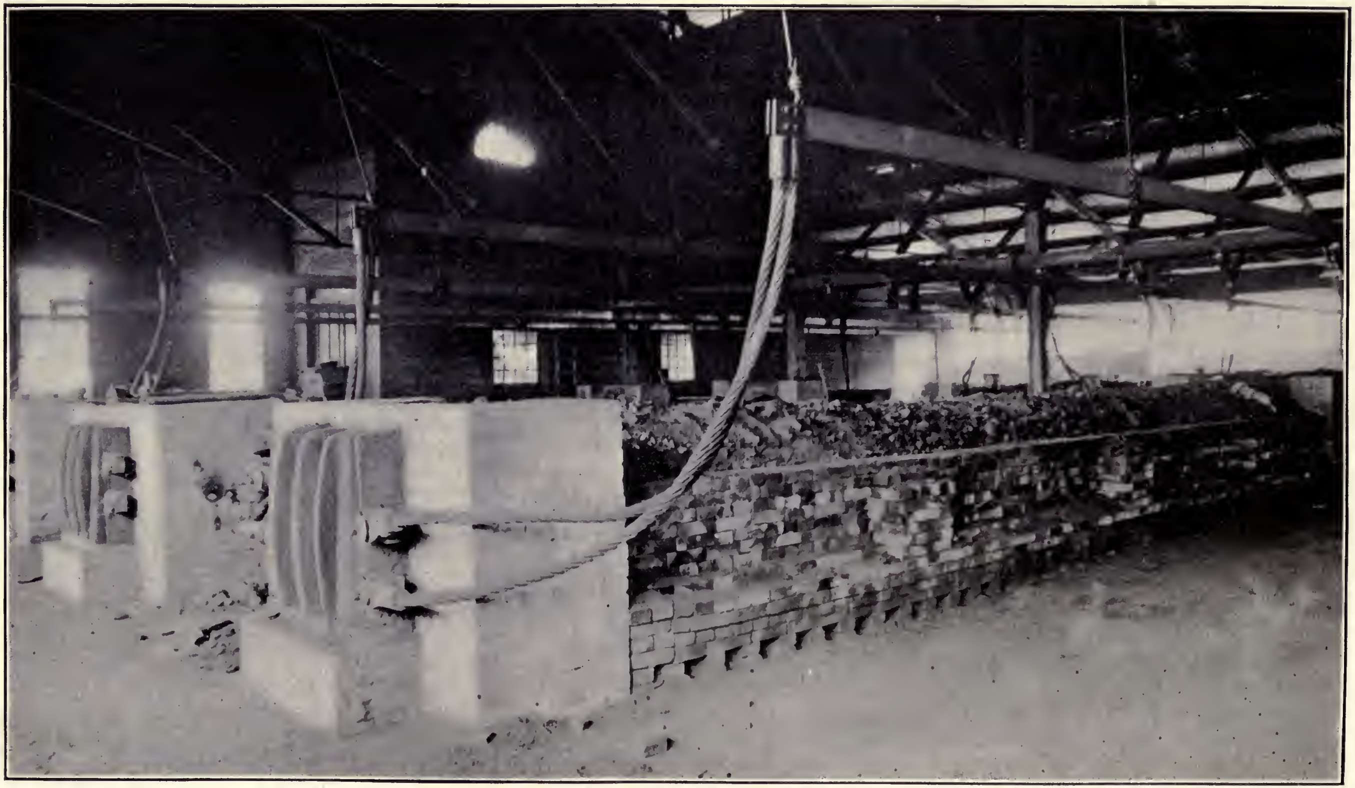

Fig. 23.—Electric Furnace for Manufacturing Acheson Graphite.

(*To face page* 143)

even more inert than any of the natural graphites. Its specific gravity is 2.25. It is ground dry and air-floated to an exceedingly fine state of subdivision and of great uniformity in size of the individual particles.

Its amorphous character renders it far less repellent to the oil than the natural graphites containing approximately the same percentage of carbon. This quality causes it to remain in place in the oil, and it is not as easily moved out of position by the drying action of the vehicle, as is the case with a high-carbon flake-graphite.

Acheson graphite used with a boiled-oil vehicle will set in the coating without the aid of any inert substance to hold it in place while drying. Used with raw oil, it requires a drier to secure the initial set of the paint, particularly if the coating is to be an external one exposed to the vicissitudes of weather.

Its manufacture is entirely unlike that of any other pigment, and is shown by Fig. 23, illustrating the style of the special electric furnace used to produce it.

In manufacturing graphite in this way, anthracite coal is heated several hours in the electric furnace by means of a powerful electric current, approximating 1000 horse-power of energy. The temperature of the mass of coal is raised to a point where the carbon is converted into carbides of the various constituents of the ash, which in anthracite coal are very evenly distributed. The temperature is then carried to the point where the carbides are decomposed, and the principal constituents of the original ash, silicon, iron, sulphur, aluminum, etc., are driven off as vapors.

The residue removed from the furnace is carbon in the form of graphite, perfectly free from any trace of the amorphous carbon or coal from which it was produced. Its method of manufacture is probably a duplication, upon a small scale, of the process by which the natural graphites were formed in the earth. The purity of the product depends upon the temperature to which it has been raised; for commercial purposes, it contains about 90 per cent of carbon. The 10 per cent of ash still remaining in the carbon is practically as inert as the graphite itself, and intimately associated with it. The furnace product is broken up, and the grades suitable for various purposes separated. The grade used for a pigment is pulverized to an impalpable powder, and air-floated for collection. In the latter stage it contrasts strongly with the poorly ground and coarse particles of many of the mineral-graphite pigments, and like a properly made lampblack or a sublimed-lead product, it has the physical character for an ideal paint.

Unfortunately, there is no standard for a graphite paint as there is for a pure-white or red-lead paint. The consequence is, that where graphite paint is specified by the engineer, he is to an extent working in the dark, and does not feel at all sure but that the coating will be spread from some one or other of the many abominations under the guise of "mixed paint," that has not an atom of graphite of any kind in it. Reputation of the manufacturer or dealer in graphite pigments or paints is quite as essential as in the case of the lead and zinc products. Adulterations in a graphite-mixed paint are more easily concealed from the eye than in those having a lead or zinc base, and are equally, if not more, annoying to the engineer.

CHAPTER XIV.

BESSEMER PAINT.

A SPECIAL pigment, claimed to be of the inert class, has lately come into use to replace oxide of iron as a straight paint for ferric structures. During the short period it has been upon the market, its use has been attended with many favorable results. It is a German development, and is reported to be the pulverized slag from Bessemer basic process steel furnaces. It is claimed to be free from the sulphur and phosphoric acid elements that are usually present in iron-oxide pigments.

It is prepared as a mixed paint ready for use. The finely pulverized furnace slag is ground in linseed-oil containing a small amount of one of the copal resins that makes the paint coating very elastic even after long exposure to the sun.

It is claimed to spread easily, covering 1000 square feet per gallon; but to do this the use of short bristle brushes is recommended, the effect of which is to rub out the coating very thin. But however closely the paint may thus be forced into contact with the surface being covered, it cannot be as well protected as where the paint is spread by long bristle brushes, and a sufficient amount of painters' labor and time is given to spread the coating. The pigment is not so deeply embedded in the vehicle, nor so well protected or bonded to the coated surface as it is when spread over a smaller area.

Bessemer paint in its natural color is a very dark gray, though it can be made a lighter shade by the addition of other substances (not of its own nature) to tint it. In this case the coating will be no more durable than the life of the most perishable pigment in the paint, as is the case with all compound paints.

Bessemer paint weighs 12½ pounds and costs $1.50 per gallon, and is claimed to dry in 24 hours without the use of added driers, which seems to indicate that the vehicle carries an energetic drier not natural to a linseed-oil and copal vehicle, as the pigment has no drying quality different from that of any iron-oxide pigment. The quick drying of the coating is also aided by atmospheric exposure, but when the slags are pulverized, these features will not protect any associated pigment or substance from the action of the atmosphere. All slag pigments are electro-negative to the metallic base pigments, and to all of the metals that constitute a part of their composition, also to the metallic surface that is coated with them.

Insulating qualities are claimed for Bessemer paint; but other paints free from metallic oxides also have this quality. The insulating qualities of any paint are due to the vehicle more than to the pigment, with the single exception of india-rubber. In any case, a paint coating cannot resist electrical currents of high potential; to moderate or low potential the insulation would be more or less resistant according to the amount of resinous matter in the vehicle. In this respect Bessemer paint, containing as it does a small amount of fossil resin, would be better than a paint containing none.

Common resin or resin oil should not be substituted for copal; they are not desirable elements in a paint, as they dry hard and crack the coating or cause it to crumble and rub off after a short exposure in the open air or sunlight, and they promote corrosion. (See Paint Tests, Chapter XXIX.)

Pulverized mineral wool has been proposed for a pigment. It is a furnace slag riven when in a molten state by a current of steam. But merely pulverizing it imparts no protective value to it for a pigment. It is acid in reaction, electro-negative in character, and when used for covering steam-pipes or other ferric bodies, on becoming damp is a virulent agent for promoting corrosion. A sample of mineral wool analyzed by Prof. Egleston, of Columbia University, gave the following result:

Substances.	Per cent.	Soluble in Water.	Insoluble in Water.
Water	1.08	1.08	
Potash	0.19	0.19	
Soda	1.75	1.75	
Magnesia	19.82	0.12	19.70
Lime	26.56	1.61	24.95
Sesquioxide of iron	0.64	....	0.64
Alumina	7.84	....	7.84
Silica	38.97	....	38.97
Sulphur (mostly as a sulphide, probably, of calcium)	2.64	0.32	2.32
	99.49	5.07	94.42

The composition of this slag is not much different from the preceding analysis of blast-furnace slag, and with it may be taken as representative of this class of substances.

No analysis of the Bessemer pigment is given by the manufacturers of the paint. It is, however, supposed to be a tetra-basic phosphate of lime, containing about 20 per cent of phosphoric acid and 50 per cent of lime, associated with other mineral and metallic substances in Bessemer iron ores. Some of these substances are partially consumed in the working of the furnace, and the balance fluxed off as Bessemer basic slag.

Bessemer basic process steel was made by the Pottstown Iron Co., of Pottstown, Pa., for a few years previous to 1893, and the pulverized slag was sold for a fertilizer. Since 1893 the basic process for making steel has been suspended in America, and the slag is now procured from Germany.

ANALYSIS OF BESSEMER CONVERTER BASIC SLAG.

Phosphoric acid	21.37	per cent.	
Lime	45.26	" "	
Iron oxide	12.00	" "	Equal to 8.40 per cent of metallic iron.
Silica	5.10	" "	
Magnesia	5.90	" "	
Alumina	4.01	" "	
Soda and potash	0.80	" "	
Manganese oxide	5.56	" "	
	100.00	" "	

An analysis of blast-furnace slags, the mean of 2000 samples from furnaces working on gray forge pig iron, is given for a comparison with the Bessemer converter slag.

Silica	43.07	per cent.	
Lime	28.70	" "	
Alumina	14.83	" "	
Iron oxide	2.83	" "	Equal to 1.98 per cent of metallic iron.
Peroxide of magnanese	1.37	" "	
Magnesia	5.46	" "	
Potash	1.84	" "	
Calcium	1.01	" "	
Sulphur	0.89	" "	
	100.00	" "	

Specific gravity 2.8 to 3.2. Fracture vitreous, similar to broken earthenware. Color dark gray, tending to the darker or brownish shades.

Blast-furnace slags are acid in reaction, while Bessemer slag is basic or neutral. Both are pyrogenic bodies unaffected by heat or sunlight, and neither is oxidized by the atmosphere.

A German chemist* gives the analysis of Bessemer paint, as known to the trade in Germany, as follows: "The pigment contains baryta, alumina, iron oxide, lime, silica, zinc oxide, sulphuric acid, carbon dioxide, and phosphoric acid." No definite percentages of these substances are given in the analysis, nor any mention whether they were separate constituents of the paint assembled in the process of grinding and mixing, or that any number of them were found combined together as a single pigment. "Graphite or other carbon is used as coloring matter, and linseed varnish as the vehicle, turpentine constituting the drier. The presumptive constitution is, therefore, lithopone, or silicious calamine ore, containing baryta and chalk, together with graphite or other form of carbon, and linseed varnish (with probably turpentine as a drier). When treated with hydrochloric acid it disengages sulphureted hydrogen."

There are many formulæ for compound pigment paints in this country, each of some declared excellence by the manufacturers of them, if not by the users; but it is difficult to select one that for the varied composition will equal this German product. Whatever may be the composition of the American brand of "Bessemer paint," it appears, from the above description, to be wholly unlike that of its German namesake, and is certainly superior to it for a ferric paint.

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* "Andes' Iron Corrosion."

CHAPTER XV.

NATURAL-ROCK HYDRAULIC CEMENT.

Hydraulic-cement coatings, either in the form of a plaster coat laid on by a trowel or as a wash or brush coating, have not been much used for the protection of ferric structures as a substitute for paints, though its use as a protection from corrosion of iron embedded in masonry is common and its value for this purpose under certain conditions is recognized.

Hydraulic cement made from the ground mineral varies greatly in quality, its general composition after calcination, that makes it caustic and anhydrous, being:

Lime.......	50 to 80 per cent	Specific gravity, 1.5 to 1.6.
Clay.......	25 " 40 " "	
Iron oxide..	3 " 14 " "	

Silica, sand, magnesia, sulphur, and many metallic oxides are also present in some amounts in many varieties of the hydraulic mineral, all of which affect the quality of the cement unfavorably when it is used for a mortar, and are more objectionable when it is to be used for a coating on ferric bodies.

The adulteration of mineral hydraulic cement is generally, from the same class of minerals of inferior quality, with free sand, silica, and iron ores containing sulphur in the form of sulphides, and all are imperfectly roasted and pulverized.

Their setting quality and strength are very irregular and uncertain whatever their trade name, or the manufacturer's report of the large quantities sold.

Analysis of an average brand of the so-called Portland cement:

Silica	(SiO_2)	20.36	per cent
Lime	(CaO)	61.90	" "
Alumina	(Al_2O_3)	7.26	" "
Magnesia	(Mg.O)	3.10	" "
Iron oxide	(Fe_2O_3)	3 24	" "
Insoluble residue	(clay and sand)	0.44	" "
Sulphur anhydride	(SO_2)	1.36	" "
Carbonic anhydride	(CO_2)	0.33	" "
Water	(H_2O)	1.97	" "
Soda Potash	(Na_2O) (K_2O_3) and loss	0.04	" "
		100.00	" "

Tensile strength of the neat cement at the end of 7 days equals 613 pounds; at the end of 28 days, 800 pounds; with one part of cement and three parts of sand for the same periods, 228 and 360 pounds.

The composition of a natural-rock hydraulic cement from Chattanooga, Tenn., is

Silica	22.17	per cent.
Lime	65.68	" "
Alumina	8.20	" "
Magnesia	1.45	" "
Oxide of iron	2.50	" "
	100.00	" "

It is a natural Portland cement similar in character, but superior to that found at Boulogne, France. The Chattanooga deposit is in the form of layers, and is over 50 feet thick. After calcination at a white heat, the following are the average results from a number of tests of briquettes.

After an exposure of one hour in the air and 23 hours in water, the tensile strength averaged 235 pounds. After one day in the air and 6 days in water, 623 pounds. After one day in the air and 27 days in water, 797 pounds. It is the strongest natural-rock cement in the world.

Portland cements are commonly made from a dual combination of the following substances:

1. Limestone with from 18 to 20 per cent of clay.

2. Chalk and clay. Marl and clay.

3. Clay-bearing limestone (argillaceous limestone) with clay, shale, or slag sand.

These substances are pulverized and mixed in some proportions that vary with the different manufacturers. The mixture is then calcined to nearly the point of fusion, or to actual fusion, forming a cinder which is finely pulverized and called Portland cement.

Furnace slag, the waste product from blast-furnaces (see Analysis, Chapter XVI), is also used as the base of Portland cement.

The slag is heated in mass and quenched in water to granulate it, making slag sand; then dried and mixed with about one-fourth part of slacked lime, and hen finely pulverized to form the cement. Slag sand usually contains from 0.5 to 1.5 per cent of the sulphide of iron, that has a tendency to oxidize on exposure to the air, which action is destructive to cement in above-ground situations. Slag cements are from 6 to 8 hours in setting, as against 1 to 3 hours for the American brands of mineral cements under test of a one-pound needle.

The color of slag cement is a delicate lilac or almost white. If the slag sand has been roasted prior to pulverizing, it is generally of a dark color similar to the ordinary brands of dark Portland cement. If a greenish color is present in the cement, it denotes the presence of a large quantity of the sulphide of iron. This greenish color is also found in some brands of the ordinary Portland cement, where the substances from which it is made contain iron sulphide, and when there has been a deficiency of heat in the oxidizing flame of the kiln.

Slag cements, when mixed and exposed to the air, must be well covered, else they will crack, though they harden under water without swelling or any material change in volume. They are completely hydrated during the process of manufacture, do not require aging, and do not deteriorate in storage.

The character of furnace slag and all the processes of its manufacture into cement require as close attention to secure a reliable product as is required for the mineral or Portland cements. The engineer should select a cement for a wash coating for ferric surfaces, or for a mortar, by its properties, *not its name*, and should require the standard he desires to reach to be met by systematic and rigid tests of every invoice of the cement, and many tests from each invoice, during their mixing and application, regardless of the names on the package.

The nature of the cement has much to do with its effectiveness. The quick-setting cements require the most care in their application, and are generally the best for ship work. If the thin cement wash once sets in the bucket it will not again set if stirred up—it is then useless. Constant stirring of the paste is necessary, as fifteen to twenty minutes after mixing suffices for it to set if not kept constantly stirred.

The Portland cements set slower than the American or natural mineral cements. Quicklime is sometimes added to delay the setting, but renders the cement more caustic and destroys the protective qualities of the vehicle in the underlying paint, and opens the way for moisture in the cement to reach the metal, and all of the coatings soon peel or flake off either from the corrosion of the iron or by the destruction of the bond between it and the paint.

Cement coatings, unless spread where they are freely exposed to a circulation of the air, are damp, and being porous, are not proof against the penetration of gases or liquids. If by accident they are exposed to the action of any copper scales, scrap-metal, or water charged with acid or alkaline substances, the soluble salts of copper thus formed will penetrate the coating, deposit the copper upon the iron or steel surfaces, set up a galvanic action, and corrode the metals beneath the cement coating.

The hardness and rigidity of cement coatings render them liable to flake off the metallic surfaces under strains due to changes in temperature of the metal that the cement cannot follow. Such places, though of minor extent, are generally inaccessible, and are quickly corroded; this action being hastened by the difference in potential between the exposed metal and the cement coating, even under ordinary atmospheric conditions. It is more rapidly developed if acidulated solutions or vapors are present, as they nearly always are aboard ships.

All of these disadvantages in the use of cement can with proper care be in a great measure lessened, if not altogether avoided. Cement coatings are in many cases the only protection that can be used to prevent corrosion, or to arrest it, even where it has progressed to an extreme or dangerous point.

Wrought-iron and steel inlet, stand-pipes, towers, and other parts of water-works metal, are subject to virulent corrosion. The usual oil-paint coatings are so soon destroyed by the effects of water in motion as to be nearly useless; and this is especially the case if the paint is iron oxide or if it has been spread over mill-scale.

The collapse of many stand-pipes shows in nearly every case that corrosion was the principal cause of their failure, as its progress at one or more places had reached such a degree that it only needed a small extraneous disturbance to wreck the structure. A case in point is that of the 60-inch-diameter wrought-iron inlet-pipes 300 feet long, and the lower sections of the stand-pipe of a large waterworks erected in 1860 and in use only a few years, when corrosion had developed upon the inner surfaces of the pipes in so many large spots and blisters, in such an irregular manner, that the engineer reported "that over one-half of the strength of the pipes to resist external pressure had been destroyed. Parts of the pipes were unaffected, the mill-scale and shop-marks being in place, while nearly one-half of them presented an appearance of being inoculated with poison."

The inlet-pipes being buried in river-silt containing a large amount of clay, were comparatively unaffected, though below the water-level; but it was still water, not subject to motion like the suction and force sides of the pipes.

The inside surfaces were scraped clean as possible, and then coated with one coat of neat hydraulic cement from $\frac{1}{4}$ to $\frac{3}{8}$ inch thick, laid on by a trowel by house-plasterers.

The water-tower was wrecked by a tornado in 1890, and all the pipes were found free from rust in any degree, and probably would have lasted indefinitely.

Imported Portland cement was used on one part of the pipes and Louisville cement for the rest. The former set slowly and had an indifferent adhesion to the iron. The Louisville cement set promptly and was easier to apply.

Many other instances of the successful use of hydraulic cement in similar situations could be cited. The quality of the cement, the manner of mixing and applying it, and the personal equation of both the engineer and the employé, are factors for success. Failures of cement coatings are more frequent than successes for the reason that in their application one or more of these requirements have been neglected.* Prof. J. M. Porter of Lafayette College divided a sam-

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* "Notes on Cement Masonry." By I. N. Knapp, Gas Engineers' Pro-

ple of a well-known and reliable Portland cement into nine parts, and sent each to a different physical laboratory with the request that tests be made of it in a mortar, one part cement to three of sand, according to the rules recommended by the committee of the American Society of Civil Engineers. The resulting average strengths reported from each of the nine samples were as follows: 75, 102, 114, 136, 153, 163, 176, 225, 247 pounds tensile strength per square inch. Average for all the samples was 153 pounds, and the lowest strength was but 30 per cent of the highest.

If these results produced by experienced men in permanent laboratories vary so much with the same cement, what is to be expected from the inexperienced and careless laborers who are generally employed to mix and apply concrete, mortar, or cement coatings?

Neat hydraulic-cement coatings crack, they set so rapidly that there is always a probability of their setting before the workmen can spread them, and the tendency of the workmen to "*knock them up*" when they indicate setting or have set, instead of mixing a fresh batch, is almost irresistible, the result being a coating of very uncertain character,—streaks of firm and close-clinging cement alternating with those of dead cement, that readily yield to a slight change in the temperature of the metal or covered surface, or to a slight mechanical injury or a frost. A strong heat from the sun also causes them to flake off.

Bad milling and insufficient burning are a frequent cause of poor cement, also an excess of magnesia in the limestone or added adulterant. Magnesia causes a chemical change or disintegrating action in the cement when wetted in the mixing. Free, natural sulphate of lime is a dangerous impurity. A low specific gravity and a dark-brown color are indicative of poor burning, and are easily detected.

For the protection of iron or steel beams or grillage, laid as the foundation or structure work below the water-line to be embedded in cement concrete, the metal should be bright and free from mill-scale, which is an electro-negative element, and with the moisture present, is certain to produce a galvanic couple with the iron it covers and promptly start the corrosion, that will proceed uninterruptedly so long as any metal is left for it to act upon. Every atom of the red rust as it forms, being also electro-negative, increases the galvanic

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ceedings American Gas Association, New York Meeting, Oct. 16, 1902. *American Gas Light Journal*, Nov. 10, 1902, pp. 665–673.

energy on the remaining metal. The rate of this corrosion will probably reduce the beams in less than one hundred years to a condition where their strength to sustain any incumbent load will be no greater than an equal quantity of tan-bark.

No paint coating on the metal can resist the galvanic action, and it should be applied solely to prevent any slight corrosion that may occur from the time the metal is cleaned until it is laid *in situ.*

A lampblack and oil, or a graphite paint are good anti-corrosive coverings, but best of all coatings for these situations is a refined bitumen and dead-oil mixture *applied hot.* Oxide of iron, or any other coating containing electro-negative substances that induce corrosion under atmospheric conditions, will only add to the strength of the galvanic couple, by bringing their oxidizable elements into the field. The nature of the soil in which the metal is directly in contact will also contribute to the corrosive action through the galvanic couple, blue clay or solid rock only excepted.

Concrete, as generally laid, is very porous, and is seldom so proportioned, mixed, or rammed in place as to enable it to fill the voids in its mass, and capillary action will enable the moisture and soil acids to reach the metal. In all such foundation work the cement should be of the best quality, free from sulphur elements, the filler should be of small size, and the sand absolutely free from salt or sea-sand in order to minimize the dangers of corrosion. These precautions are seldom if ever taken, even in part, much less as a whole. The neglect of these particulars will soon be apparent in the failure of many an important structure whose life will be measured by a few decades instead of centuries. That the corrosion in these cases is out of sight and mind and irreparable will be the more aggravating.

Porosity of Hydraulic Cement.

In a general way, engineers and architects are inclined to blindly trust hydraulic cement in many locations where in parallel cases it has failed. The quality of a cement suitable for a concrete block would not be advisable in a wash coating for a wall or to bed an anchor bar. All hydraulic cements are not only porous but permeable.* Quay walls laid in beton blocks, composed of about 440 pounds of Portland cement to each cubic meter of sharp clean sand and mixed

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* Excerpts from a Report of M. M. Leon Durand Claye, Engr. in Chief of Bridges and Roads, Paris. "Annales des Ponts et Chausées," May, 1888.

with from 300 to 440 pounds of water, the walls being surmounted by ashlar masonry, were disintegrated in less than a year by the action of sea-water. There was a movement or change in the character of the beton, even when 660 to 880 pounds of Portland cement per cubic meter of sand was used. In parts of the work where they had not been exposed to the action of sea-water, the beton of all proportions of cement and sand were not only very porous but very permeable. Under a head of about three feet, the permeability was indicated by a rapid fall of the water in the vessel where the beton block was under test. *The permeability of the cement was in all cases accompanied by a disintegrating effect in the beton.* The disintegration was found to be due to the formation of perceptible quantities of the sulphate of lime by the action of the sea-water on the Portland cement. The sulphate of lime, when formed in the mass of concrete, solidified more or less completely in crystals of such a nature as to develop considerable molecular activity. Some of the beton cement analyzed .75 to .80 per cent of sulphuric acid.

The greater the amount of water used to mix the cement the greater was the permeability and porosity of the concrete, even with all proportions of the cement and sand. Mortar made with 7 per cent of water was very permeable, and this increased perceptibly as the percentage was increased to ten and eleven. In all cases where sea-water instead of fresh water was used to gauge the cement, the bad effects in the mortar were at once apparent.

Prof. Bauschinger's experiments showed that the adherence of a first-class Portland cement to a *bright* wrought-iron floor beam was 625 pounds per square inch; that mixtures of two parts of fine, sharp bank sand to one of cement reduced the adhesion to about 70 per cent of the above value. In mixtures of three parts of sand to one of cement the adhesion value was less than 50 per cent. That with each increase in the percentage of sand from the above amounts, the reduction in strength and adhesion was very rapid. The quality of the cement had a great effect upon the adhesion value. In the commercial cements usually provided for contract concrete, the adhesion was frequently only 20 per cent of that given above.

Bloxam's "Chemistry," edition 1895, pp. 376, 377, states "that the ordinary corrosion of iron is accomplished only in the presence of moisture, air, and CO_2. If any of these substances are absent the corrosion cannot take place. The reactions are:

$$Fe+H_2O+CO_2=FeCO_3+H_2. \quad . \quad . \quad . \quad . \quad . \quad (d)$$

The $FeCO_3$ is dissolved by the carbonic acid present, and the solution absorbs oxygen from the atmosphere, in accordance with

$$2FeCO_3+O=Fe_2O_3+2CO_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The Fe_2O_3 combines with the moisture and is deposited as $2Fe_2O_3.3H_2O$, or ordinary iron rust. Iron in its ordinary state is not affected in perfectly dry air, and it will not rust in water containing a free alkali or alkaline earth or an alkaline carbonate, because the affinity of these alkaline substances for *any acid* is greater than that of iron, so that they would neutralize the acid before it had time to attack the iron."

This neutralizing action, however, would only be effective for a short time or until the alkaline substance became saturated with the acid element. There are no locations where concrete is used or cement coatings applied to iron for its protection from corrosion where *reviving* the saturated alkaline substance is possible. It is therefore only necessary to have a limited amount of some acid present with air and moisture to cause the ultimate destruction of a large amount of iron, because the CO_2 or other acids present never become fixed, but are always active, passing from molecule to molecule, as long as there is any free metal for them to attack.

It is proposed to increase the safeguard afforded by alkaline substances to delay corrosion by mixing the concrete, mortar, or wash coating with whitewash instead of plain water. The small amount of lime thus added to the cement does not materially detract from its strength.

Slag cements, because of the sulphides present, should be avoided for use in concrete or any coatings in contact with iron. It is hardly possible to assemble them with an amount of any alkaline substance that will permanently neutralize the acid element present in their composition, aggravated in nearly every instance by the porous nature of all concrete constructions caused by deficient ramming to fill the voids occupied by the enclosed air, also by the surplus of water used in mixing.

Even a cement free from the sulphur element, if mixed with a small quantity of cinder, or if laid in soil containing cinders or pyrites, will absorb the acid and collect it in dangerous amounts in the voids of the concrete. Once there, it will ultimately reach the metal and cause the failure of the grillages by the columns or other superincumbent load punching through the foundations. These conditions are further aggravated by the fact that nearly all ground-water is charged to some extent with saline or sulphur elements or both, that would soon saturate any alkaline substance present in the cement. When this point is reached corrosion of the grillage will inevitably ensue even if the imposed columns show no evidence of its action.

Grillage ironwork has been removed from concrete foundations laid only five years and found to be corroded $\frac{1}{8}$ inch or more over its whole surface. The thickness of grillage beams is seldom $\frac{1}{2}$ inch, so that thirty or fifty years will practically limit the safety of many of the modern steel skeleton structures.

The protection afforded to steel by Portland cement has been subjected to experiment by Prof. Charles L. Norton.* "Two brands of American cement were selected, tested chemically and physically and found to be good. A sharp, clean bank sand and fragments of trap-rock and flint were thoroughly washed and used for the concrete. The cinders *were washed* and dried; they tested distinctly alkaline with a small amount of sulphur. All the ingredients were mixed dry in every case, and when wet with a minimum amount of water were tamped until they flushed.

"Briquettes were made in duplicate with both cements, viz., neat cement, one part to three of sand, one part to five of broken stone; cement one part, two of sand, and five of stone; cement one part, sand two parts, and five of cinders. Specimens of mild-steel rods $6'' + \frac{1}{4}''$ diameter, mild sheet-steel plates $6'' + 1'' + \frac{1}{32}''$ thick, and strips of expanded metal $6'' + 1''$ were all cleaned bright. All three pieces were put into each briquette and were enclosed in separate tin boxes, which also contained a specimen of each metal unprotected. One-half of the briquettes were set in water for one day and the rest for seven days before sealing them up tight. One-quarter of the boxes were then subjected to each of the following exposures. To an atmosphere of steam, air and carbon dioxide; to air and steam; to air and carbon dioxide, and the other samples set upon a table in a room with no special care as to their temperature or dryness.

"At the end of three weeks the briquettes were cut open and the steel examined and compared with the specimens which had lain unprotected in each of the tin boxes.

"The specimens covered with neat cement were as bright as when placed in the briquette, the cement had prevented any trace of corro-

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* Engineer in charge of the Insurance Engineering Experiment Station, 31 Milk Street, Boston, Mass. Excerpts from Third Report, 1902.

sion, while the unprotected samples consisted of more rust than steel. Of the remaining specimens hardly one had escaped serious corrosion. The location of the rust spot was *invariably coincident* with either a void in the concrete or a badly rusted cinder. Rust had as usual produced rust.

"In the more porous mixtures the steel was spotted with alternate bright and rusty areas, each clearly defined. In both the solid and porous *cinder* concrete many rust spots were found, *except where the concrete had been mixed very wet, in which case the watery cement had coated nearly the whole of the steel like a paint and protected it.*

"Some briquettes made of finely *ground* cinders and cement in varying proportions up to one of cement to ten of cinders and exposed to moisture and carbonic acid showed how effectually the presence of the cement prevented rusting, provided there were no cracks or crevices or distinct voids. The corrosion found in cinder cement appeared to be mainly due to the *iron oxide* in the cinders and not to the sulphur. Cinder concrete, well rammed when wet to fill the voids, is about as effective as stone concrete in protecting steel."

These latter conclusions would depend greatly upon the absence or low percentage of iron oxide and sulphur in the cinder. To render these elements inert to iron, there must be enough free alkaline substance in the cement to saturate the acids without disturbing the general composition of the cement as a binding element.

If the metal is painted before the application of the concrete, whatever its composition, the continuous void left over the whole surface of the metal by the decay of the paint is the best possible condition for inaugurating corrosion. Air and moisture will find ready access to this void, also to the voids left by building bricks and terra-cotta blocks, the porous nature of which are favorable to the condensation and absorption of moisture and atmospheric gases, that are more highly charged with corrosive elements in cities, tunnels, subways, and other locations where the use of structural steel work is in most demand.

How far the protection of ferric foundations, either near or below the water-line in the many structures already built, or in progress in all parts of the world, has been considered by their architects and engineers time only will reveal. For those proposed, like the miles of rapid transit and railway tunnels, a great portion of which will be carried through ocean silt or salt-marsh mud and exposed to the most virulent form of corrosion, some more positive and effectual means of protection from corrosion must be employed than *has ever* been adopted. No wash or trowel coating of cement, good or bad, or applied in mass, will avail for but a short period to protect the metal that these structures must rely upon for a great part of their strength.

The hardness and inelastic character of cement or mortar coatings will cause them to crack under the vibrations inevitable to all railway structures; and while resisting water in mass, they will absorb moisture sufficient to be always damp and in that condition are of the least strength.

The wires of the anchorage ends of the cables of the Niagara Falls suspension bridge were opened for a short distance where they entered the anchorage pits. These ends were embedded in hydraulic cement, and at the end of forty years many of them had become so corroded that the strength of the structure was seriously impaired. The corroded strands were replaced by new wires, and the top part of the anchorages opened to allow the cement work to dry out and remain dry. In this case and with all ferric material embedded in concrete, the caustic action of the usual make of cement, whether damp or wet, will furnish the carbonic acid necessary to destroy any linseed-oil coating or paint that covers them and induce corrosion. The subsequent drying out of the cement coverings only delays for a short time the ultimate destruction of the metal.

Iron anchor bars and chains embedded in concrete below the water-line for 100 and 200 years were free from rust when removed. Fresh-water immersion, no access of air, no acid element nor iron oxide or calcium sulphate, also no voids in the cement was the secret of their perfect condition.

The present method of constructing buildings wholly or in part of steel framing and concrete, avoiding the use of brick and stone masonry as far as possible, is causing a great deal of anxiety among architects and engineers as to the future state of the metal so embedded. That metal needs some additional protection from the caustic action of the impure cements too frequently employed, also from the quicklime mortar, beyond the usual coat of paint, is recognized.

At a late meeting of the English Architectural Association, Mr. H. Humphrey gave as the result of his experience that metal buried in concrete containing furnace cinders or coke breeze, should be coated with Dr. Angus Smith's anti-corrosive compound, or some other compound containing pitch and sand; that some samples of cinder concrete analyzed as high as three-fourths of one per cent of sulphuric acid. A case was cited by another member of the association where a hot-water pipe laid in cinder concrete was rotted away in a very short time.

The cinder concrete used in the floors of the steel-frame skyscrapers in New York City invariably shows the presence of sulphuric acid strong enough to redden litmus-paper.

Gas-pipes embedded in plaster of Paris (gypsum) have been found to be completely corroded in a few years. The use of gypsum in cement to hasten its setting is detrimental. Gypsum is soluble to some extent in water, besides it contains water from its hydration, which absorbs carbonic acid from the air that quickly causes corrosion. The rust so formed absorbs moisture and carbonic acid and further hastens the corrosion.

The screwed ends of all pipes are invariably attacked. They are of bright metal only about $\frac{1}{16}$ inch thick and seldom, if ever, have even a brush coating of any paint to protect them when put up or left in place. Galvanizing the fittings and body of the pipes does not protect the screwed ends; the corrosion at these points is only hastened by the galvanizing.

The effect of corrosion upon the floor beams and other structural parts used in modern architectural work has been the subject of discussion by the American Society of Architects, the concensus of their opinion being expressed by one of the prominent members as follows:

"With regard to the strength of the steel-cage constructions, both as to wind strain and other disturbing strains, there is no question. All objections arising from these points have been overcome, but unless exceptional care is taken in the construction to protect the steel cage, particularly at its joints, from corrosion, this class of buildings will not be permanently safe. It is perfectly feasible, with great care, to protect the steel frames from corrosion, but I am convinced that many high buildings have been put up in this country where the proper care in this respect has not been taken nor the necessary preventives against corrosion applied."

On the 12-inch steel I beams carrying the sidewalks around the Pabst Hotel in New York City, and that were removed after being in place less than six years, corrosion was in active progress. The space beneath the beams was used as a café, always dry and heated.

Wherever the brickwork came in contact with the beams in all of the stories, the paint was dead and corrosion established. This was particularly noticeable in many portions of the beams where the usual top dressing of coal cinders had been laid to level up the arches forming the foundation for the artificial stone sidewalk. The rivets that held the corner angle-irons to the beams were nearly all loose from the corrosion around their heads or points and had lost their set or draw.

In marine work, hydraulic cement is used almost exclusively as a brush coating on the inside surfaces of the ship's frames and plating in the lower holds of the vessel where the metal is exposed to the action of bilge-water, alkaline and acid solutions from acids, and leakage from the cargo liquids. One or more wash coatings of cement are applied over the red-lead, black-varnish, or other oil-paint coating laid on during the construction of the ship, and that generally serve to protect the metal during this period. The coatings in the lower part of a ship are damp by reason of the confined saturated sea air, but the cement (if good) forms a close, clinging coating that seldom fails unless by mechanical injury or improper mixing or application, and is easily repaired if injured.

The confined spaces aboard a ship almost preclude the use of an oil paint or varnish, however quick drying it may be, without the use of forced ventilation to provide the oxygen necessary in the drying of paint. Such ventilation is practically impossible in a ship at sea, or in most cases in dry dock.

Cement for rendering, with the object of making brickwork watertight, should be mixed with an equal part of absolutely clean sand free from salt or sea-sand. Cement for any use should be carefully turned over by the shovel and exposed to the air before being mixed or wetted.

Brickwork is one of the worst surfaces to hold a paint, good or poor. A hard-burnt brick will absorb 8 ounces of water, a salmon brick nearly 11 ounces. Brickwork absorbs most of the oil in the paint, leaving the pigment on the surface of the bricks without sufficient bond to hold it, and it peels in strips. This peeling is hastened by the caustic action of the cement or lime mortar and the soluble salts in the sand of the mortar, which soon destroys the organic matter in the oil.

The soluble salts in the bricks and mortar often cause a white efflorescence to appear on the surface of the wall shortly after being built. This cannot be brushed off, but it disappears during wet weather and returns again when the wall is dry, and is only dissipated after many rain-storms. The composition of the efflorescence varies. The chlorides of calcium, magnesium, and sodium sulphate and oxalate of lime are generally present; all of which are hygroscopic and form a germinating place for fungi, one of which, the *Penicilium crustaceum*, is represented by Fig. 24.*

Walls a year or more old are less troubled with the efflorescence or by the peeling of the paint from the fungus.

FIG. 24.—Photomicrograph × 600 of *Penicilium crustaceum.* This is the greenish fungus which makes calcium oxalate on brick walls. (M Toch.)

When walls are freshly laid or plastered the surfaces can be prepared for painting by applying a solution made of twelve fluid ounces of sulphuric acid in a gallon of water and repeating the application when the first one appears dry. Allow the coatings to stand for a day or two, then rinse off with clear water, and when dry prime and paint as usual. This process changes the lime in the mortar and cement from a caustic carbonate to a neutral sulphate of lime; also produces a uniformly absorbent surface free from spots that are more porous than the general surface, or that contain lumps of improperly slaked or mixed lime. The surface so prepared takes the paint easily and well and does not blister nor peel.

If plastered surfaces a few months old be washed with a solution

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* Maximilian Toch (New York City). *Journal of Chemical Industry* (London), Vol. XXI, No. 2, Jan. 31, 1902.

of 2 ounces of bicarbonate of ammonia in a gallon of water, as soon as dry the oil priming or painting can be done without danger of peeling.

A silicate of soda solution made from equal weights of silicate and warm water, and applied with a brush, is also recommended for preventing the peeling of paint on walls, but for outside exposures it is not so effective as the above acid treatment.

Waterproofing Bricks and Sandstone. At a recent meeting of the Australian Association for the Advancement of Science, Professor Liversidge read a paper on the "Waterproofing of Brick and Sandstone with Oils." Experiments were made with the view of ascertaining the length of time that brick and sandstone are rendered waterproof or protected by oil. The oils used were the three commonest and most readily obtainable for such purposes, viz., linseed-oil, boiled linseed, and the crude mineral oil known as "blue oil," used for preserving timber. The weatherings were made upon a flat portion of the laboratory roof fairly exposed to the sun and weather. Good, sound, machine-made bricks were experimented on. The amount of oil and water taken up by the sandstone was very much less than that absorbed by the brick, although the area of the sandstone cubes was much greater than that exposed by the bricks. Equal amounts of raw and boiled oils were absorbed; the blue oil, however, was taken up in much greater quantity by both brick and sandstone, but by the end of twelve months the whole of the 13½ ounces of blue oil had apparently evaporated and the brick had returned to its original weight. The bricks treated with raw and boiled oils remain unchanged. After the second oiling in November, 1890, and exposure for nearly four years and two months, they had practically retained all their oil, inasmuch as they had not lost weight, and were also nearly impervious to water. It was noticeable that the sandstone cubes treated with raw and boiled oils returned to their original weights, but did not appear to have lost the beneficial effects of the oils, being also practically waterproof.

Portland or other hydraulic cements free from the sulphate of lime, when mixed with about 15 to 25 per cent of a red-lead paint, forms a tough elastic coating that dries hard enough to resist the action of locomotive exhaust steam and cinders on the surfaces of iron beams, trusses, and the buckle-plates of low headway bridges. It is also damp-resisting to a great degree, and can be coated over with other paints with some measure of confidence that they will not peel.

A special damp-resisting paint, known as the "R. I. W." (trademark), has proven of merit in many instances of its use in very unfavorable situations. From a government analysis of it, the composition is approximately 30 per cent of an oil vehicle, 65 per cent of refined special bitumen and selected fossil resins, and 5 per cent of a carbon pigment. It is laid on or spread like a thin coating of mortar on brick masonry or plastered walls. It adheres firmly, becomes very tacky, and can be plastered over with cement or lime-mortar coatings that adhere firmly. When these plastered coatings are dry they can receive an oil paint of any desirable color, unaffected by dampness from the walls.

A grade of the "R. I. W." is also made to apply to damp walls not intended to be plastered, also to iron structural work. This is applied with a brush, and contains more pigment than the trowel grade. It is thoroughly damp-proof, and receives oil-paint coatings without any tendency to craze them or to peel.

A grade of this composition, to be spread with a brush on the inside of tanks where acid and alkaline solutions are stored, effectually resists the action of these liquids. In chemical works for the protection of the ironwork and other metals, it has shown great resisting power. A special instance of the waterproofing character of this compound to resist the action of running water under a considerable head is on the concrete monolithic water-power house on the St. Lawrence River at Massena, N. Y., where several thousand square yards each of the trowel and brush coatings were applied, and completely corrected the porosity and permeability of the cement walls that were seriously endangering the structure.

Herr Wm. Cremer, superintendent of the gas-works at Enskirchen, Germany, states: "That the ammoniacal liquor from gas-works, even in the weakest solutions, detrimentally affects the cement and tank-walls exposed to its action. Coating the surfaces thus exposed with liquid glass (tungstate of soda) protects the cement, also renders the surfaces quite leakage-proof even in very old work."

CHAPTER XVI.

BOWER-BARFF COATINGS.

"*Bower-Barff*" is the name given to the rustless coating formed upon cast iron, wrought iron, and steel, when exposed to a low red heat in special ovens, furnaces, or retorts, and subjected to the action of superheated steam, carbonic-oxide gas from coal-fires or gas-producers, hydrocarbon and hydrogen gas alternately or in combination, according to the several processes invented by Bower-Barff, Wells, Gesner, and other inventors.

The original inventor of the rustless iron coating was Prof. Frederick S. Barff, of Kilburn, England, who published an account of his process in 1876, and read a paper describing it before the Society of Arts, London; but the process did not prove commercially successful on account of its high cost and the difficulty of obtaining uniformity in results.

Messrs. George and Anthony Bower, of St. Neats, England, improved the process of Prof. Barff, and patented it. The right to use it in the United States was acquired by Mr. George W. Maynard, of New York. The first furnace was erected at the Hecla Architectural Iron Works, in Brooklyn, N. Y.

The next and most important of the improvements in this process was invented and patented in 1888 by Mr. W. T. Wells, of Little Ferry, N. J., who discovered that red-hot iron, in the presence of mingled steam and carbonic oxide, would form the magnetic or black oxide (rustless coating) of iron, Fe_3O_4, without the intermediate formation of the sesquioxide, Fe_3O_2 (red rust), the reactions being, $3Fe+4H_2O. =Fe_3O_4+4H_2$. This process is the foundation for all subsequent improvements of the process and is applicable to all forms of cast, malleable, wrought iron, and steel where the surfaces are not to be subjected to hard friction or wear, such as bending, hammering, chipping, or other rough usage.

The protection of the metal being due to the conversion of the surface of the metal to magnetic oxide, and not any material alteration of the metal which would weaken it, it follows that any manipulation that would injure the continuity of the coating must necessarily destroy the coating. Wherever the coating is broken the metal will rust, though the rust will be localized, and will be greater than the same exposure of the metal not coated, owing to the difference in potential between the two surfaces.

These rust-spots seldom spread or raise the adjacent coating, as is commonly the case with paint, or enamelled coatings. All drilling, fitting, screw-cutting, etc., of the metal should be done before it is put into the converting-oven. In riveting, the oxide in the immediate neighborhood of the rivets will be broken, and bolting together of parts to be connected together must be substituted. In work that is riveted up before being coated, the set or draw of the rivets will be released by the heat of the furnace. This, in the case of light grill, lattice, or fence work, is possibly of small moment, but in work subject to the action of liquids or gases it cannot be ignored and other methods of joining the pieces must be adopted. Shearing, flanging, sharp bending, or driving of nails through sheet-iron roofing, necessarily exposes the metal, and local corrosion of the injured part follows. The bite of the vise or pipe-wrench in fitting rustless screwed steam- or water-pipes injures the coating unless special care and tools are used to prevent the injury. The screwed ends of pipes and fittings are injured if the joints are made up dry, but with red lead, graphite, or other good pipe-joint cements as lubricants, they seldom give trouble if moderate care is exercised in the work.

In cast-iron pipe with bell and spigot joints, the lead packing can be calked without injury to the "rustless" coating by using the round-nose calking-tool, instead of the usual sharp-edged tool that chips the coating. Rustless pipe coatings do not appear to draw in the lead joint any more than the usual coal-tar dip coatings, from the changes in temperature that all pipes are subjected to when buried in the ground.

The mechanical finish of the metal to be coated determines to a great extent the mode of treatment. Articles in the rough, from which the skin has not been removed, require a longer exposure, higher heat, and a more energetic oxidation than those whose surfaces are more or less machined or finished; the latter requiring lower heats. A high heat on a finished surface tends to blister and detach the oxide as fast as it forms. Ordinarily, only the rust and mill-scale are removed by scraping and use of steel brushes. Where a handsome appearance of the oxidized ware is desired, the surfaces must be cleaned by the sand-blast, or by pickling, and the same care used to remove all traces of the pickling acid by a warm lime-water bath and repeated washing with cold water-jets under pressure, as in the case of cleaning the metal for painting (Chapter XXVIII). Foundry-sand upon castings, if not removed, bakes in the furnace to a reddish-brown color, producing unsightly spots, but does not impair the rustless character of the coating, and unless the coating is to serve as a finish, without being painted, the spots are of no moment; otherwise the sand must be removed to the clean-scale surface before treatment. All blow-holes and other defects in castings must be plugged with brass or iron plugs. Lead or other soft fillings are detrimental to the action of the furnace in producing a reliable or fine-appearing coating, which should be a pleasing blue-gray or blue-black color. If the metal is polished before treatment, it acquires a lustrous ebony-black finish, very desirable upon certain kinds of articles.

The iron or steel articles treated, owing to the annealing action while in the furnace, are permanently expanded about $\frac{1}{24}$ inch per foot, for which allowance must be made where this addition will be repeated, as in stair-stringers, columns, etc.

The limit of elasticity of the oxide coating is practically the same as that of the metal it covers. The coating adheres firmly under tensile, torsion and compressive strains, until the elastic limit has been reached, and no further.

In Sir Joseph Whitworth's tests of specimens of Bower-Barffed wrought iron, submitted to tensile strain, small pieces of the oxide coating scaled off when the strain reached 28,618 pounds per square inch, or beyond the elastic limit, and about one-half of the ultimate strength of the specimen. In the case of cast iron, the coating remained in place uninjured when strained to the point of rupture.

Bower-Barffed articles can be heated to temperatures approximately 400° Fahr. and then immersed in cold water without injury. They resist the action of sea air, sea water, sulphurous, and other gases, ammonia, and all alkaline and organic acids in moderate solution, also the caustic action of lime and hydraulic cement either dry or damp. They are, however, affected by strong solutions of sulphuric and hydrochloric acids.

A comparative test of the resistance to corrosion of a number of protective coatings under different exposures resulted, viz.: *

CHANGE IN WEIGHT OF WROUGHT AND CAST IRON WITH DIFFERENT PROTECTIVE COATINGS AND UNDER DIFFERENT CONDITIONS, IN POUNDS PER SQUARE FOOT OF SURFACE PER ANNUM.

WROUGHT-IRON SHEETS (NO. 23 GAUGE, BLACK).

Protective Coatings.	Exposed to the weather Inland.		Immersed in—		Average gain.
	Canada.	New York State.	Fresh water.	Sewage.	
Bower-Barffed	.0	gain, .000.3	.006.7	.003.6	.002.5
Tinned	gain, .002.0	" .000.1	.019.4	.007.1	.006.2
Nickel-plated	.0	" .000.5	.050.4	.003.1	.013.5
Galvanized	gain, .000.4	.....	.045.9	.080.5	.042.0
Barffed	" .001.0	gain, .003.1	.083.9	.117.0	.051.2
Black—*i.e.*, unprotected	" .001.3	" .022.6	.137.0	.169.0	.082.5
Copper-plated	" .000.2	" .005.0	.179.0	.182.0	.091.6
Average gain	.000.2	.005.1	.074.6	.080.3	.040

CAST-IRON PLATES.

Protective Coatings.	Exposed to the weather Inland.		Immersed in—		Average gain.
	Canada.	New York State.	Fresh water.	Sewage.	
Bower-Barffed	gain, .004.0	gain, .003.1	gain, .005.5	.001.4	gain, .002.8
" " and paraffined	" .000.6	.001.9	" .000.2	.008.4	" .002.8
Galvanized	.0	.0	" .049.1	.061.0	" .027.5
Tinned	.....	gain, .003.1	" .065.5	.061.0	" .041.1
Nickel-plated	gain, .003.4	" .002.5	" .131.7	.083.3	" .053.5
Copper-plated	" .004.0	" .005.0	" .150.8	.119.2	" .067.8
Black—*i.e.*, unprotected	" .006.3	" .012.0	" .148.3	.272.4	" .106.6
Average gain	.002.9	.002.1	.007.2	.086.7	.041

The cost of applying the process must necessarily vary with the size, weight, and other characteristics of the article to be treated. For builders' hardware and that class of articles called shelf goods, domestic articles, etc., the cost is about 5 per cent of the net cost of the goods to the manufacturer. Wrought-iron grilling, office railings, and the better class of scroll and fancy work cost about two cents per pound. Wrought-iron steam and water-pipe is coated for about the same expense per pound as is required to paint it. A further benefit to this class of articles is, that the inside of the pipe

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* Trade catalogue. "Rustless Iron and Steel. The Bower-Barff and Wells Processes." (Pamphlet Number V. Illustrated.) By the Bower-Barff Rustless Iron Company, New York, 1896.

receives the same coating as the external parts. Wrought-iron I beams, channels, and other shapes entering into building constructions can be treated very cheaply; the principal expense is first cost of the furnace; the actual operating expenses are very small—fractions of a cent per pound.

*The Iron Column of Delhi.**

The iron column of Delhi, India (see *Frontispiece*), is 20 feet high above ground, 16 inches in diameter at the base, and 12 inches at the top, with an ornate Persian capital 3½ feet in height. The base has a Persian inscription of six lines on the western side, symbolizing the deeds of the Rajah Dhawa, who reigned in the ninth century B.C. Beck, in his "History of Iron," places its erection in the early part of the fourth century A.D., but other authorities place it in the ninth century B.C., corresponding to the inscription upon it.

Early excavations to the depth of 26 feet did not reach the bottom, but subsequently it was found to rest upon forged-iron beams, bedded and anchored to the stone foundations. A short distance below the ground it is 2 feet 4 inches in diameter, and evidently was forged from a large number of wrought-iron blooms. Its estimated weight is seventeen tons.

It stands alone above all other relics, a monument commemorative of the state of the mechanical arts in prehistoric times, not only for its construction and preservation, but its transportation from some unknown and evidently far-distant place of manufacture and its erection *in situ.* This would be considered, at the beginning of the twentieth century, an exceedingly creditable example of engineering skill, and it will probably remain centuries after most of the present-day ferric constructions have crumbled to red rust.

It is free from corrosion, and while this in a measure may be due to the climate of India not being inducive of corrosion, it cannot alone be the reason of its protection, for other iron articles, both large and small, bear testimony to corrosive effects under the same exposure and climate. A reason for its non-corrosion has been given: that in the earlier days following its erection it was considered a part of the religious duty of every pilgrim to the holy shrine near which it is located to climb it, and as the pilgrims annointed their bodies with oil as a part of their devotional exercises, that more or less of this oil was

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* *Iron Age*, August 1, 1895, p. 215.

left upon the column and thus protected it. But for the past two hundred years or more, so far as known, no such greased-pole gymnastical devotions have been practised, and the coatings of oil, if any ever were thus applied, must have long since been dissipated, as they would doubtless have been palm or some other vegetable oil or camel's fat, all of a non-siccative nature.

The ornate capital is as free from corrosion as the shaft of the column, so unless the pilgrims climbed this as well as the shaft (as a sailor-boy mastheads his ship's truck), and possibly stood on their heads as a further sign of exalted zeal, the capital could not have received the oil treatment to protect it. The part of the column underground surely had no such acrobatic oleaginous distribution, and is comparatively as free from corrosion as the part above ground. Every indication in the appearance of the column shows that after it had been forged and finished, the inscriptions and capital still bearing the chisel-marks on the ornaments, it was subjected for its entire length to a process identical to that of the modern Bower-Barff process, which has proven to be quite as effective to prevent corrosion in this instance as in any of the modern examples of this protective method.

CHAPTER XVII.

GALVANIZING. ELECTRO-CHEMICAL AND OTHER ANTI-CORROSIVE ZINC PROCESSES.

*Galvanizing.**

Galvanizing to protect the surface of large articles, such as enter into the construction of railway viaducts, bridges, roofs, and shipwork, has not reached the point of appreciation that possibly the near future may award to it. Certain fallacies existed for a long time as to the relative merits of the dry or molten and the wet or electrolytical methods of galvanizing. The latter was found to be too costly and slow, and the results obtained were erratic and not satisfactory, and soon gave place to the dry or molten-bath processes as in practice at the present day; but the difficulty of management in connection with large baths of molten material, the deterioration of the bath, and other mechanical causes limit the process to articles of comparatively small size and weight.

The electro-deposition of zinc has been subject to many patents, and the efforts to introduce it have been lamentable failures in both a mechanical and financial sense. Most authorities recommend a current density of 18 or 20 amperes per square foot of cathode surface, and aqueous solutions of zinc sulphate, acetate or chloride, ammonia chloride or tartrate, as being the most suitable for deposition.

Herman's process has been experimented with on a commercial scale, the chief feature being the addition of the sulphates of the alkalies or alkali earth to a weak solution of zinc phosphate.

Electrolytes made by adding caustic potash or soda to a suitable zinc salt have been found to be unworkable in practice, on account of the formation of an insoluble zinc oxide on the surface of the anode and the resultant increased electrical resistance; the electrolytes are

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* Excerpts from a paper by the author, presented at the New York meeting (December, 1894) of the American Society of Mechanical Engineers, and forming part of Volume XVI of the *Transactions*. Also *Transactions of the American Society of Mechanical Engineers*, Vol. XV, 1894, Paper No. 598, pp. 998–1073.

also constantly getting out of order, as more metal is taken out of the solution than could possibly be dissolved from the anodes by the chemicals set free, on account of this insoluble scale or furring up of the anodes, which sometimes reaches ⅛ inch in thickness.

To all intents and purposes the deposits obtained from acid solutions under favorable circumstances are fairly adhesive when *great care* has been exercised to thoroughly scale and clean the surface to be coated, and which is found to be the principal difficulty in the application of any electro-chemical process for copper, lead, or tin, as well as for zinc, and that renders even the application of paint or other brush compounds so futile unless honestly complied with. Unfortunately these acid zinc coatings are of a transitory nature, their durability being incomparable with *hot galvanizing*, as the deposit is porous and retains some of the acid salts, which cause a wasting of the zinc and consequently the rusting of the iron or steel. Castings coated with acid zinc, rust comparatively quickly, even when the porosity has been reduced by oxidation, aggravated no doubt by some of the corroding agents, sal-ammoniac, for instance, being forced into the pores of the metal. In wrought iron, the cinder is porous, and holds the acid, and induces corrosion.

The relative porosity of zinc coating, applied by different methods, is shown by the following micrographs, Figs. 25 and 26, taken from *The Engineer*, September 28, 1894.

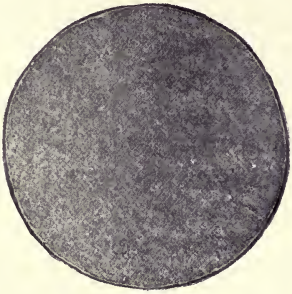

Fig. 25.—Zinc coating applied by hot galvanizing process, magnified five diameters.

Fig. 26.—Deposit from zinc sulphate solution (acid), magnified five diameters.

Other matters of serious moment in the acid electro-zincing process, aside from the slowness of operation, were the uncertain nature, thickness, and extent of the coating on articles of irregular shape, and the formation of loose dark-colored patches on the work, the unhealthy non-metallic look, and want of brilliancy and lustre prevented engineers and the trade from accepting the process or its results except for the commoner articles of use.

The Cowper-Coles process of electro-zincing articles claims to overcome all these difficulties, and plants are in process of erection with a bath of some 14,100 gallons capacity, capable of turning out forty tons of light work per week, and in which it is proposed to treat the plates of vessels sixty feet in length upon one or both sides, and the frames of such vessels as torpedo-boat destroyers and kindred craft after riveting up. These plates and frames are given a thin coating of zinc by this process that appears to be perfectly uniform in character and extent whatever the shape of the piece may be, and however numerous the lugs, flanges, mortises, or core-holes. It is called "*zinc-flashing*"; that is, coating the iron or steel article, after pickling and cleaning, with a thin coat of zinc about one ounce per square foot of surface, which resists the inclemency of the weather and mechanical injury as well as a thicker coat, and is found to afford sufficient protection in most cases, and is adequate protection until such time as it is ready to receive the usual paint coatings.

To obviate any tendency of the paint to peel from the zinc surfaces, as it generally manifests a disposition to do, it is recommended to coat all the zinc surfaces, previous to painting them, with the following compound: One part chloride of copper, one part nitrate of copper, one part sal-ammoniac, dissolved in sixty-one parts water, and then add one part commercial hydrochloric acid. When the zinc is brushed over with this mixture, it oxidizes the surface, turns black and dries in from twelve to twenty-four hours, and may then be painted over without danger of peeling. Another and more quickly applied coating consists of bichloride of platinum, one part dissolved in ten parts distilled water and applied either by a brush or sponge. It oxidizes at once, turns black, and resists the weak acids, rain, and the elements generally.

There are also a number of trade-mark, or proprietary, mixtures to prevent the peeling of paint applied to zinc. "Uniter," an English compound, and "Galvanum," an American paint in light-brown and dark-gray colors, are favorably recommended. Carbon and asphaltum paint, containing a large percentage of bisulphide of carbon in the vehicle, also adheres well to galvanized iron. Its nauseating odor and highly inflammable character during its application are strong points against its use.

Galvanized-iron sheets that are corrugated after galvanizing corrode more rapidly than uncorrugated sheets. Sharp angles and twists in the sheet also corrode quickly. The thin zinc-coating atoms are brittle naturally, and are opened to allow moisture to reach the metal they cover. This being a more elastic metal, plates coated with it do not show the bending effects so strongly, yet they are apparent.

Double-coated tin, zinc, or terne plates are from two to three times more resistant to corrosion than single-coated plates. The second coating, like the second coat of paint on a painted surface, fills the shrinkage, cracks, and pores in the first coat. Galvanized-iron pipes used for gas and water service in the ground have only a life of 12 to 15 years, the outside coating of zinc being destroyed by galvanic action induced by the acid elements in the soil. If the soil contains furnace cinders, the corrosion is hastened. The screwed ends and other parts of the pipe where the galvanizing has been cut away are the parts first corroded. In general all galvanized pipework is so poorly cleaned from mill-scale and grease prior to galvanizing, that the pipes are less enduring than with a common coal-tar pitch dip coating.

Zinc surfaces, after a brief exposure to the air, become coated with a thin film of oxide—insoluble in water, which adheres tenaciously, forming a protective coating to the underlying zinc. So long as the zinc surface remains intact, the underlying metal is protected from corrosive action, but a mechanical or other injury to the zinc coating, that exposes the metal beneath to the presence of moisture, causes a very rapid corrosion to be inaugurated, the galvanic action being changed from zinc positive to zinc negative, and the iron as the positive element in the circuit is corroded instead of the zinc.

When galvanized iron is immersed in a corrosive liquid, the zinc is attacked in preference to the iron, provided both the exposed parts of the iron and the protected parts are immersed in the liquid. The zinc has not the same protective quality when the liquid is sprinkled over the surface and remains in isolated drops. Sea air being charged with saline matter is very destructive to galvanized surfaces, forming a soluble chloride by its action. As zinc is one of the metals most readily attacked by acids, ordinary galvanized iron is not suitable for positions where it is to be much exposed to an atmosphere charged with acids sent into the air by some manufactories, or to the sulphuric-acid fumes found in the products of combustion of rolling-mills, iron, glass, and gas works, etc.; and yet we see engineers of note covering in important buildings with corrugated galvanized iron and using galvanized-iron tie-rods, angles, and other construction shapes, in blind confidence of the protective power of the zinc coating; else in supreme indifference as to the future consequences and catastrophes that may arise from their failure.

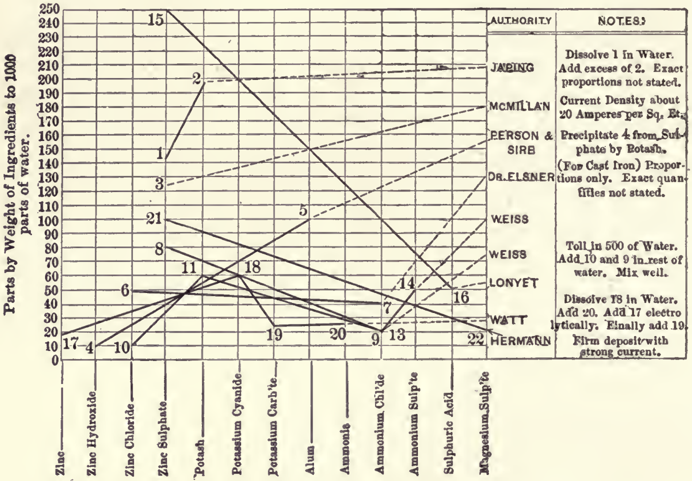

FIG. 27.—Zincing solutions recommended by various authorities.

The comparative inertia of lead to the chemical action of many acids has led to the contention that it should form as good if not a better protection to iron than zinc, but in practice it is found to be deficient as a protective coating against corrosion. A piece of lead-coated iron or terne plate placed in water will show decided evidences of corrosion in twenty-four hours. This is to be attributed to the porous nature of the coating, whether it is applied by the hot or wet (acid) process. The lead does not bond to the plate as well as either of the other metals, zinc, tin, copper, or any alloys of them. Lead-coated iron corrodes rapidly when exposed to the gases of combustion. The usual weight of lead-coated terne-plates is about $\frac{3}{4}$ ounce to a square foot, while hot-process zinc coatings weigh from $1\frac{1}{2}$ ounces minimum to 3 ounces maximum, depending upon the temperature of the bath, and the slowness of removal therefrom giving time for the article to drain off. The following table gives the increase in weight of different articles due to hot galvanizing:

Description of Article.	Weight of Zinc per Square Foot.	Percentage of Increase of Weight.
Thin sheet iron = .026 inch No. 22 B. W. G.	1.196 oz.	18.2
$\frac{5}{16}$-inch plates	1.76 "	2.0
4-inch cut nails	2.19 "	6.72
$\frac{7}{8}$-inch-dia. bolt and nut	approximately 1.206 oz.	1.00

Tin is often added to the hot bath for the purpose of obtaining a smoother surface and larger spangles or facets, but it is found to shorten the life of the coating considerably.

A portion of a zinc coating applied by the hot process was found to be very brittle, breaking when attempts were made to bend it; the average thickness of the coating was .015 of an inch.

An analysis gave the following result:

Tin	2.20
Iron	3.78
Arsenic	trace
Zinc (by difference)	94.02

A small quantity of iron is dissolved from all the articles placed in the molten-zinc bath, and a dross is formed amounting in many cases to 25 per cent of the whole amount of zinc used. This zinc-iron alloy is very brittle and contains by analysis 6 per cent of iron, and is used to cast small art ornaments from.

Nickel coatings produced galvanically will not protect iron from corrosion unless .02 inch thick.

A hot galvanizing plant having a bath capacity of 10 feet by 4 feet by 4 feet 6 inches outside dimensions, and about 1 inch in thickness, will cost $625, and will hold twenty-eight long tons of zinc, which at four cents per pound will require $2500 to fill it; the heating of this mass of metal and its ever-changing cold immersions, with the waste by dross and extra thickness in spots, is a constant source of annoyance and expense.

The cost of an electro-chemical or wet-bath Cowper-Coles plant of 6700 gallons bath, size 30 feet by 6 feet by 7 feet, will be but slightly more than the hot bath given. There is no dross formed by the use of the Cowper-Coles process, and the zinc coating formed is said to resist the corroding action of a saturated solution of copper sulphate. The English Post-office test for telegraph wire coated by the Cowper-Coles process shows much better than hot galvanized-iron wire, as per following table:

RESULT OF PROCESS TEST MADE ON SAMPLES OF CHARCOAL-IRON WIRE COATED WITH ZINC BY VARIOUS PROCESSES.

Process Used to Coat the Wire.	Grains of Zinc Per Square Foot.	Ounces Per Square Foot.	Number of One-minute Dips; Samples Stood without Showing Metallic Copper.
Hot galvanized................	648.5	1.48	3
Acid bath, $ZnSO_4$..............	446.4	1.02	4
Cowper-Coles process...........	552.64	1.26	5

A Cowper-Coles process bath of a capacity of about 4000 gallons will treat ship-plates 18 feet long, and will require an electrical energy of 2000 amperes of 5-volt electro-motive force.

With equal amounts of zinc per unit of area, the zinc coating put on by the cold process is more resistant to the corroding action of a saturated solution of copper sulphate than is the case with steel coated by the ordinary hot galvanizing process; or, to put it in another form, articles coated by the cold process should have an equally long life under the same conditions of exposure that hot galvanized articles are exposed to, and with less zinc than would be necessary in the ordinary hot process.

The hardness of a zinc surface is a matter of some importance. With this object in view, aluminium has been added from a separate crucible to the molten zinc at the moment of dipping the article to be zinced, so as to form a compound surface of zinco-aluminum, and to reduce the waste formed from the protective coverings of sal-ammoniac, fat, glycerine, etc. The addition of the aluminum also reduces the thickness of the coating applied.

Cold and hot galvanized plates appear to stand abrasion equally well. The thickness of the coating being the same, tests by means of the Schlerometer show: cold galvanized sheet, 6; hot galvanized sheet, 6; terne-plate, 2; tin-plate, 2. The figures represent the load in grammes upon a diamond point, just sufficient to cause it to scratch the specimen.

The attempts to electro-zinc iron and steel wire for wire standing rigging, bridge, or other cables have not been successful; it has not been found practical to produce a wire capable of withstanding more than one immersion in a copper-sulphate solution.

Both pickling and hot galvanizing reduce the strength, distort and render brittle iron and steel wires of small sections. Zinc fuses at 775° F. and vaporizes at 830° F. Hence the necessity of the sal-ammoniac bath that covers the molten zinc, prevents volatilization and acts as a flux to unite the zinc and iron. The bath is usually kept at about 1000° F. Steel wire of high breaking strain has its hardness, and consequently its ultimate tensile strength and elongational efficiency, reduced by drawing the temper and the formation of an iron zinc alloy on the surface of the wire by as much as from 5 to 10 per cent. It is the practice when coating steel wire to keep the bath at as low heat as possible and to run the wire through it at a high rate of speed. Both these operations lead to a waste of zinc by reason of the rapid solidification of the metal on the comparatively cold wire, and consequently the ready breaking or cracking of the covering metal on bending or twisting it, owing to the difficulty with which molten zinc adheres to the steel except after long contact in the bath. In some cases the wire is wiped between asbestos rubbers as it leaves the bath, but wire thus treated is found to resist corrosion but a very short time.

Table Giving Thickness of Zinc Required to Withstand Varying Number of Immersions in a Solution of Copper Sulphate.

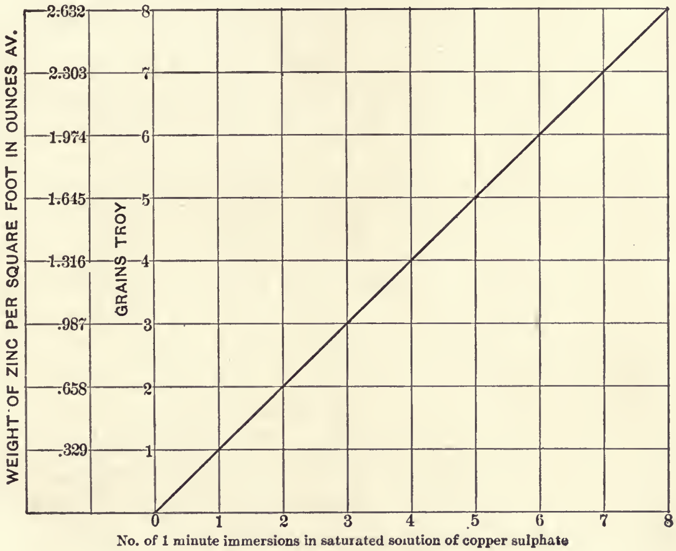

Fig. 28.

English manufacturers have ceased galvanizing their high-grade steel wire that costs some $175 per ton, on account of the great risk of rendering it worthless.

The Cowper-Coles or cold-galvanizing process is used for the purpose of zincing the skin plates and frames of the torpedo-boats and torpedo-boat destroyers built for the English navy. A plan and elevation of this plant is given in *The Engineer*, Feb. 28, 1894.

The industrial importance of the successful application of this cold-galvanizing process can hardly be overestimated, even if its application is only to the marine constructions of the future, and it is found to be in any degree inapplicable to our present structures and vessels in use. The permanency, continuity, strength, and density of the coating given by this process is in all respects equal to that of hot galvanizing, and the thickness of it can be made superior to that given by the hot. Considering the success that has attended the use of zinc to prevent corrosion in marine boilers, where concentrated hot saline fluids are the excitant medium, aided by the electrical conditions attendant upon the combustion of large quantities of fuel, it may not be considered a wild prophecy to expect that with all of the internal metallic parts of a steam vessel protected by an application of zinc plates secured to the framework of the structure similar to the application of zinc to marine boilers, that these plates may receive the energy of corrosion, and if not neutralizing it entirely, at least pass it along in the form of a deposit to convenient pockets, where it could be removed, the same as is now done with the washings and dirt from the fire-room bunkers and ballast-chambers.

This internal electro-chemical process of protection does not appear so chimerical as at first one might suppose. Dr. Henry Wurtz * has proposed the protection of mining plants subject to the intensified corrosion due to the decomposition of pyrites and other minerals in the mine waters, by connecting all of the metal portions of the mine as the negative elements with a dynamo of sufficient force to overcome the strength of galvanic energy due to the surfaces exposed being excited by the corrosive liquids in the mine, the positive terminal to be connected to a mass of hard coke in the mine sump. These conditions vary but slightly from those existing in the ship, and it is not improbable that experiment will determine that both these systems could be made to work successfully.

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* *Engineering Magazine*, May, 1894, Vol. VII, No. 3, page 297, "Preservation of Metals from Corrosion by Electric Polarization."

Thermo-electric currents arise from changes of temperatures in all bodies, and set up voltaic action in all cavities, fissures, seams, and contact surfaces in the metal, which, though slight and not easily detected, will in time enlarge and waste them away sufficiently to sap the strength of the mass.

Metallic salts and acids in mine waters intensify the corrosion of all metals exposed to their action. The metal work of railway tunnels is also disastrously affected by the condensed vapors of sulphur, carbonic acid, and the ever-present moisture due to such locations. The corrosion of the metals decreases the resistance of the water to voltaic circuits, this corrosion by liquids being voltaic phenomena in all cases. In many cases it is intensified by the moisture being in the form of drops instead of being uniformly spread over the whole surface.

Acids and acid salts which are capable of taking up iron oxides into solution still further enhance the destruction by removing such oxides and exposing the surfaces of the metal to a fresh attack of the corrosive element. The saline matter in solution that excites voltaic action need not be acid. Any *neutral* salt which decreases the resistance of the water will qualify it to act as the necessary liquid medium of a voltaic circuit. Sea-salt is the commonest of all such neutral salts, together with the other chlorides and sulphates of sea-water. It enables corroding voltaic action to be set up on all ferric bodies immersed therein or in the air impregnated with their substance.

The Journal of the Society of Chemical Industry, London, February 28, 1894, details some experiments with the galvanic action of sea-water upon iron and steel structures in various relations with each other, such as the constructive parts of trusses, boilers, etc., to prevent the corrosion for which the use of zinc and other easily oxidized metals and alloys are suggested, and to be so placed and connected to the structure that they will form the electro-positive element of the ever-present galvanic circuit, and by their decomposition protect the structure.

Mr. D. Phillips, in a paper read before the Institute of Civil Engineers, in 1885, cited the result of an experiment, where "surfaces of bright pieces of plate iron, immersed in cold sea-water for over ten years have been thoroughly protected from corrosion by the aid of pieces of metallic zinc in metallic contact with the iron; while a similar piece of iron similarly fitted and immersed, but having a piece of paper placed between the iron and zinc plate, received no protection whatever. The water was changed twice annually, and the oxide removed from the zinc by filing. Under these circumstances the iron became gradually coated with a film of leaden-colored deposit when wet, but hard and white when dry. The effect in other respects was that, on every occasion that the oxide was removed from the zinc and the deposit from the iron specimens, on being returned to the water small globules formed on the zinc, and on reaching $\frac{1}{10}$ inch in diameter released themselves and flew to the surface."

The proportions necessary to insure complete protection from corrosion in marine boilers are one square foot of zinc to fifty square feet of heating surface in new boilers, which may be diminished after a time to one in seventy-five or even one in one hundred square feet. Merely placing the zinc in trays, hangers, or strips *will not* insure metallic contact. The better and generally recognized method of fixing the zinc is to place a number of studs in the sides of the furnaces and combustion-chambers, and to bolt on to these studs the zinc plates, which should be about 10″×6″×1″. It is important to see that the contact surfaces are clean and bright, and the nut screwed close down to the zinc to exclude the water and deposits from the contact surfaces, thus comparatively insulating them and preventing the galvanic action. Otherwise the zinc is acted upon mostly as a solvent that renders the water innocuous or non-exciting, but does not prevent the water from forming a hard scale when it is saturated.

Sheet zinc has proven to be a durable roofing material. Zinc is reduced in density from 6.86 to 7.2 in the process of rolling into sheets, which closes the pores and renders the metal less affected than tin-plate from the ammonia, carbonic acid and atmospheric gases.

Berlin zinc roofing-plates (unpainted) have been found to be not materially affected after many years' exposure. The weather formed a thin film of oxide on their surfaces that effectually prevented further oxidation. A few cases reported are as follows.

The Cloisters of Canterbury were covered with zinc roofing and were uninjured after 33 years.

The Portsmouth Dock Yard Buildings' roofs were uninjured after 24 years. The Great Western Railway Station roof at Rugby was uninjured after 20 years. Other railway-station roofs were uninjured after 15 to 20 years. The zinc roofing required painting if sulphurous acid was in the atmosphere.

Tin roofing corrodes from the inside of the coating. It is also porous, quite as much so as a single coat of paint. The tin-plate as it leaves the molten dipping-bath becomes covered with a thin film of fluxing or non-drying oil that fills the pores of the tin, and if the roofing is painted soon as laid, this film prevents the paint from adhering to the tin, just as a machine grease prevents a paint from bonding to a surface. A few months' exposure to the atmosphere slightly oxidizes the tin, and this oxide absorbs the oily coating and allows the weather to wash it away and the paint has a clean metallic surface to bond to. Tin-plates doubly dipped are less porous and more durable.

The quality of commercial tin-plate is greatly inferior to that made forty years ago, and appears to retrograde yearly. Lead, antimony, and other metals are mixed with the tin in the dipping-bath, and greatly reduce its resistance to corrosion. None of the adulterants form a true alloy; they are only mechanical mixtures. They all differ in oxidizing power and electrical affinities. The lead is electro-negative to the tin and zinc, which again are of opposite electrical natures.

The amount of sulphurous and carbonic acids and ammonia in the atmosphere is enough to form the excitant element needed to decompose them one after another, until the coating is made porous and the iron is corroded in turn. The life of the tin-plates is also governed in a great measure by the want of care that they should receive in the preliminary pickling with muriatic acid, to free them from the mill-scale that always attends their rolling. Ordinary washing with lime-water does not remove the whole of this acid, and the tin coating usually has a double galvanic pile in a sandwich form, ready for duty on the least encouragement.

There are brands of tin-plate as honestly coated at the present day, and as reliable in all respects, as any ever made, but they are an exception, not the rule. Price and the gullibility of the purchaser govern, as in many other modern industries. (See Fig. 6, page 38.)

Red-lead paint coatings soften tin roofing, but do not wholly destroy it, although some of the tin may be changed to a white oxide that is easily removed by atmospheric influences.

CHAPTER XVIII.

INERT PIGMENTS, OR ADULTERANTS.

The different substances known as inert pigments are used to a great extent in the preparation of nearly all mixed paints, particularly in the house paints, where the amount of one or more of them frequently exceeds that of the base pigment.

However admissible their use (on account of cost only) may be in paints not classed as protective ferric coatings, their durability in any case is determined by the character of the weakest element in the associated group to resist atmospheric conditions, whatever the base pigment may be.

The manufacture of "*patent paints*" would be almost nil were it not for the very liberal use of these inert pigments. They are said to correct almost every detrimental quality in the basic pigments. Yet with all of their boasted virtues, there is hardly a manufacturer of paint willing to admit their use, or that will furnish an analysis of his product that contains them.

Many of the uses and characteristics of these *inerts, fortifiers, or adulterants* have been mentioned in the basic pigments chapters and elsewhere in this work, but are brought together here for comparison and ready reference.

Carbonate of lime ($CaCo$) in some form other than as quicklime (calcined limestone or marble) is often used as a desirable adulterant of many paints. It is claimed to be specially favorable to correct the sulphur element present in iron oxides.

Chalk is a friable carbonate of lime that, on account of its cheapness and several colors, is the most used. Its specific gravity is 2.2 to 2.8. According to the basic oxides in it, the colors are white, red. gray, and black. It contains about 2 per cent of clay besides free silica, magnesia, and chloride of calcium, and carries a large quantity of water. The latter is loosely held, and as calcination of chalk is not thought necessary when used for an adulterant, the moisture is carried into the paint to its detriment.

Whiting. Spanish white and other trade-name whites are preparations from chalk. When used to correct the sulphur element in iron-oxide paints, 10 per cent by weight of the pigment is often added. It is as easily dissolved by moisture as whitewash. Its use for the adulteration of white-lead pastes or paints is common rather than exceptional, and frequently composes 50 per cent of the paint. Whiting, when used as a pigment, is liable to form a chemical reaction between the oil and itself that results in the formation of a lime soap, which is not at all a durable substance.

Putty, however (a mixture of whiting and oil), is a very durable body, and withstands atmospheric exposure and water remarkably well. In this form it illustrates the theory that the pigment is the life of the paint. The small amount of oil in the composition of putty is the cause of its quick drying. Its mass, when applied, greatly exceeds that of a paint coating, and its shrinkage solidifies, instead of rupturing it, by a movement in a number of directions, as in a paint.

Barytes (*Heavy Spar*), $Ba.SO_4$. Specific gravity, 4.3 to 4.7. The natural sulphate of barium, consisting of one atom of barium oxide $(BaO) = 65.67$ per cent, and one atom of sulphuric acid, 34.33 per cent. It is the heaviest of all minerals, and is found in all stages of purity, in transparent, colorless, white to yellow crystals, also in a granular and compact form in heavy beds resembling marble. It is common in all metallic veins, allied with, or changed to, calc-spar, spathic iron ore, cerussite, quartz, limonite, pyrites, and other substances. It is the white variety that is ground for a pigment, but lacks the opacity or light-reflecting or coloring power to form of itself a good pigment. It grinds hard, splintery, and irregular, and is used to give weight to paper-stock, zinc oxide, gypsum, and all the other light pigments that lack weight to enable them to masquerade as white lead. (See Chapter VI.)

Barytes brightens light-colored paints, though of poor coloring or light-dispersing power; also spreads easily and saves oil. It is mixed with nearly all pigments, and by the use of a stiff or short bristle brush, covers a large surface with a resemblance of a good paint.

White lead does not cover so well with barytes, but zinc oxide covers better. Zinc oxide lacks weight that barytes furnishes and also saves oil, advantages not ignored by the cheap paint-compounders. Barytes does not unite with the oil in any degree. From its weight and non-bonding nature, the paint is inclined to run on vertical surfaces. This tendency requires the use of large amounts of volatiles or quick driers. Barytes alone is the poorest of pigments.

Floated barytes is the ground natural sulphate of baryta floated off in water to give a finer product.

Artificial barytes (Blanc-Fixes) is made by heating barium carbonate with sulphuric acid and precipitating the artificial barytes from the solution. It is less crystalline than the natural sulphate and has a greater covering power.

Baryta white, permanent white, constant white, etc., are of this class of pigments. Blanc-Fixe mixed with the mineral barytes compose the principal substances in most of the commercial white patent paints.

Lithopone, a trade-mark for one of these mixtures, has an extended sale under the guise of white lead. Trade-marks are easily invented, but they add no durability to the paint. They move around in paint literature as easily as some of the substances covered by the name move in the vehicle that gives them a home, if not rest.

Barytes as a pigment, exposed to air or on underground bodies, condenses water and carbonic acid and is converted into a carbonate with the evolution of sulphuretted hydrogen. This decomposing feature in barytes seems to be ignored by paint-compounders, but to it the failure of many coatings can be attributed.

Rose's experiments show that barytes in any form, when acted upon by water, evolves sulphuretted hydrogen and sulphurous acid, leaving the decomposed lime free.

Hansfeld has also shown that sulphate of lime is decomposed by the galvanic action of two metals or metallic oxides in contact under the ordinary exposures of a paint. When both barytes and gypsum are present in a paint, this galvanic action between three substances *is certain to occur*. Mixtures of barytes and gypsum with the oxides or carbonates of zinc or lead will in no degree protect any one of them. They decompose one after the other; the first to break down only adds to the electrolytic energy to hurry up the decomposition of the others. The thin film of oil in which the pigments are embedded is sufficiently porous to admit the atmospheric moisture and carbonic acid necessary to start up the disintegrating process.

Putty made from barytes, whiting, and oil dries into a hard, brittle mass that crumbles easily. Glycerine added to it only temporarily defers the extreme shrinkage and crumbling.

Probably the greater number of the mixed white-lead pastes and paints sold in the world contain barytes; as it costs only $10 to $20 per ton, or about one-sixth as much as white lead or zinc oxide, the temptation to use it in place of these pigments is not always resisted. As a rule no responsible paint firm with a business reputation to sustain will sell a barytes adulterated paint under their name.

Additional data about the presence of barytes in a paint is given in Chapter XXIX. The covering and coloring power of barytes in comparison with white lead and zinc oxide are shown by Fig. 29.

FIG. 29.—Covering power of inert pigments.

Brick-dust is used to a large extent to adulterate red lead and other red paints; even the low-price iron oxides do not escape it, particularly the brighter-colored copperas oxide. It tones them down to many required trade-shades. Care is not always exercised to grind only the hard-burned bricks for the pigment, hence many of the samples are not much better than a dried clay or red chalk.

Prof. Mallett's experiments with paints composed of pulverized hard-burned red tiles, iron oxide, and red lead were favorable in certain proportions of the several substances, and decidedly unfavorable with other proportions of the same ingredients, whether applied to wood or iron. In general the tiles added nothing to the quality of the paint, only reduced the cost of it. They are practically unoxidizable by atmospheric influences or weak acidulous solutions, and are electronegative to metals or their oxides. In any electrolytic action set up by any cause in a paint coating of which brick-dust is a part, the tendency will be to decompose the other pigments, possibly, before electrolysis is developed in the covered iron surface. (See page 53.)

Feldspar. Specific gravity, 2.5 to 2.8. Decomposed mica, granite, gneiss, and most forms of basalt form this class of adulterants, and are all inclined to further decomposition on exposure to the weather. Many of the fire-clays used in the manufacture of fire-brick are broken down and decomposed feldspars. Its use in the composition of a pigment is of the most unreliable character in all respects. It is as poor a substance for an adulterant as nature furnishes. Mixed paints frequently contain 15 to 20 per cent of it. Feldspar carries a large amount of water loosely held and frequently acidulated, also sand, etc. It is easily whipped up in the oil and mixes well with graphite for dark-colored paints.

Gypsum (*Sulphate of Lime*). Natural mineral (hydrated), $CaO.SO_3 + H_2O$; calcined, $CaO.SO_3$. Specific gravity, 2.4 to 2.8. The natural mineral ground is the plaster that farmers use on their crops to attract and condense atmospheric moisture. Calcined to expel the one atom of water held in its natural state, it becomes the common plaster of Paris, used for the hard finish of plastered walls of buildings. The process of grinding is supposed to drive off the one atom of water it holds naturally, by the heat developed in the dry grinding-mill, but this is soon replaced upon a short exposure to the atmosphere, and when used for the hard finish, it must be heated again to dispel it, or a porous wall coating results. A hydrated sulphate of lime contains over 18 per cent of water.

When used in the composition of a paint, it must be thoroughly calcined, and is so specified by parties who allow its use. Neglect of this carries the moisture into the paint, where some portion of the sulphur element in the gypsum is released, and combining with the fatty acids in the oil, sometimes causes the paint "to liver," a phenomenon familiar to all painters, but not always attributed to the right cause, viz.: too much of a sulphurous adulterant.

Gypsum grinds easily, is opaque, and incorporates readily with most pigments and the vehicle. It is not liable to set or settle in the paint-bucket or package, and probably is the best of all the inert substances to use as an adulterant.

The extra atom of sulphur in the natural mineral other than that necessary to form the sulphurous-acid compound is strongly combined, but if the mineral or ground pigment is calcined at a temperature higher than that necessary to release the one atom of water, the sulphuric-acid atoms are excited to a degree that will afterward manifest the same destructive properties as the same element does in any other pigment or substance, and as noted above in the "livering" of the green-paint coating.

A synthetical sulphate of lime is supposed to be formed when iron ore is roasted in a furnace in contact with a quantity of carbonate of lime. The roasting process, besides driving off the moisture in both the iron ore and carbonate of lime, and a part of the sulphur in the iron ore, excites the remaining atoms of sulphur to leave the ore, and combines with the now anhydrous carbonate of lime, CaO, and forms the anhydrous sulphate of lime, $CaO.SO_3$, described above. The process is an unsatisfactory one, as the carbonate is generally added in great excess of the amount needed to effect the chemical combination with the sulphur to form the sulphate. When the roasted iron ore is removed from the furnace to be ground, the sulphate is not distinguishable or separable from the uncombined carbonate of lime, and both are ground with the ore and appear as adulterants, that may be 5, 10, or 20 per cent, or as much as can be unloaded upon the consumer.

In whatever amount these lime products are present in the iron-oxide pigment, they are both, like the oxide, anhydrous, hygroscopic, and readily attract moisture, frequently 5 per cent in oxide pigments that have been made for some time.

The synthetical sulphate of lime formed in the roasting of copperas, as described in the preparation of that substance for an iron-oxide pigment, is of the same character as that from roasted iron ore, only it carries more loosely combined sulphuric acid in its composition, as is denoted by the brighter color of the pigment. Its effect upon the paint coating is the same, and is not conducive to any permanency of color or protective qualities.

Kaolin (*American Terra Alba*). A clay of the same class as pipe-clay, China clay, potters' clay, etc. The reddish color of the latter being due to the iron and other metallic oxides. Specific gravities, 2.58 to 2.76.

Their general composition is as follows:

Substances.	Pipe-clay, White.	Potters' and China Clay, Light and Dark.	Terra-Alba, White and Gray.
	Percentages.	Percentages.	Percentages.
Alumina	23.25 to 21.28	23.25 to 21.28	28.51 to 15.50
Silica	72.23 " 65.49	73.33 " 64.95	67.50 " 49.65
Lime	....	....	22.40 " 1.52
Magnesia	....	....	0.17 " traces
Oxide of iron	....	1.26 to 2.54	3.70 " 2.05
Alkaline earths	....	7.26 " 1.78	
Sulphate of lime	....	4.72 " traces	
Moisture	12.00 to 4.00	4.00 " 1.30	8.58 to 0.42

All of the pigment-clays grind greasy, and are as easily broken down and decomposed by the weather as any of the clays in building brick or mud from a mill-pond.

Mixed with talc, the clays are supposed to add some advantage to pigments of a granular character. What that advantage is the author has never been able to ascertain, but he knows they cause paint to peel or crack.

Marl. Specific gravity, 2.4. It is composed of:

Carbonate of lime	50 per cent.
Silica	12 " "
Alumina	32 " "
Oxides of iron and manganese	2 " "
Water	4 " "
	100 " "

Its gray color prevents its use as an adulterant of the white paints, but in the tinted colors it is used quite as freely as kaolin or chalk. It is difficult to pulverize on account of its greasy nature. It saves oil, but causes the coating to chalk or peel on a short exposure to atmospheric influences.

Ochre. A yellow clay containing from 8 to 15 per cent of water loosely held with large amounts of sand, also marked quantities of iron oxide and sulphur. When moderately heated, the lower grades of ochre contain sulphur enough to change their color to a pink or low red.

The common grades were formerly used as a coating for tin roofs. They were always subject to blistering, from the large quantity of water they carried into the paint. It is an adulterant without a single inert element in it, and its presence in a paint is generally accompanied by as poor a quality of oil as it is a pigment.

Silica ($Si.SO_2$). Specific gravity, 1.9, 2.5, 2.8. Is a sulphate of silicon containing one atom of silicon combined with one atom of sulphurous acid. It is found in crystals of different degrees of translucency, and forms a component part of all metallic ores; of iron ore, frequently, 50 per cent. (See Analyses of Iron Ores, Chapter III.)

In its natural form it is one of the most imperishable of all minerals. It grinds hard and splintery, and is difficult to reduce to the fineness required for a pigment. Manufacturers of silica products subject the crystals to a bright-red heat and quench them in water, causing them to fracture and grind more easily. However, the calcination drives off a part of the sulphuric acid and renders the silica caustic,—the latter condition is not a favorable one for any pigment, inert or basic.

Silica is not affected by sulphurous gases, acids, or alkalies. Floated silica or silex makes an excellent wood-filler paint. All silicas are difficult to hold up in oil, and on settling, cake very hard.

Sand, generally supposed to be the same substance as silica, is, however, of quartz formation as an oxide of silicon; specific gravity 1.44 to 1.76, only about two-thirds the weight of silica. It grinds hard and splintery, or in an irregular crystalline form, and is difficult to grind to a pigment.

Neither silica nor sand mix with other pigments, except in a purely mechanical manner, differing according to the specific gravities of the several substances incorporated together. They have no affinity for the vehicle, are not in their pulverized form absorbent of moisture, except to a very small amount. From their indestructible nature, they form the electro-negative element or centres to determine the electrolytic action always present in the decay of a paint coating. Their use as adulterants of mixed paints is greater than any manufacturer of paints will acknowledge. The covering power of silica is shown by Fig. 29.

Fine sand is used for an application to green paint on exterior surfaces with a view to affording an extra protection from atmospheric effects. It in all cases hastens the decay of the paint. It holds the moisture, dust, and other organic substances, and their easy and early decomposition results. Blisters form more readily under a sand-coated paint than with a paint alone.

Talc (*Steatite or Soapstone*). Specific gravity, 2.65 to 2.8. Grinds greasy and flaky, is inclined to cause a paint to peel, and is repellent to the oil. Its use with kaolin has been given. It is used for a special adulterant of flake and other graphitic carbons (see Chapter XIII). As a pigment it has no qualities whatever. As an adulterant its function is to enable some objectionable substance to attempt a mission that could be better performed by a straight pigment.

The above list does not exhaust the substances known as adulterants or miscalled "inert" pigments. As protective coverings for ferric bodies, the protective effects of the inert pigments in use with the basic pigments will be noted in the paint tests made to determine their value (see Chapters XXIX and XXX). Their covering or coloring powers are shown by Fig. 29.

The following amounts of inert pigments were produced and used in the United States (averaged for the years 1898 to 1901):

Barytes, all grades, 124,000 short tons. Cost of the crude mineral, $3.30 to $3.50 per ton.

Imported barytes, 1400 tons, including some floated. Cost of the manufactured article, $10.50 to $11.00 per ton.

Feldspar mined in the United States for all purposes in 1898 to 1901 averaged 27,280 tons and cost from $3 to $6 per ton.

Ground slate and shale for pigments averaged 4,700 short tons, value from $9.50 to $10.00 per ton.

Of soapstone ground for pigments and foundry use, there were produced 9000 tons yearly. Value 8½ to 9 cents per pound.

Of gypsum calcined, for all purposes, 280,000 short tons were produced in 1901, cost $3.50 to $3.90 per ton.

Crude gypsum costs $1.20 to $1.25 per short ton.

CHAPTER XIX.

SPIRITS OF TURPENTINE.

THE composition of spirits or oil of turpentine is $C_{10}H_{16}$. Specific gravity, 0.86 to 0.88, with a boiling-point always near 160° F. The several varieties of commercial turpentine obtained from the sap of fir- and pine-trees are more or less viscid solutions of resins in a volatile oil, the proportions of these constituents varying according to the source and age of the turpentine-tree. Some kinds are clear and homogeneous; others are more or less turbid, holding in suspension granulo-crystalline masses, which gradually settle to the bottom, and are known to painters as "drops."

Spirits of turpentine is the product of the first distillation of the crude gum, and consists of about one-third spirits and two-thirds water. It requires about twenty-five barrels of crude gum to make two barrels of the spirits of turpentine, that when redistilled is known as refined or oil of turpentine.

The principal supply of turpentine is obtained from the American long-leaf yellow pine-tree, *Pinus palustris* (*P. australis*); also from the loblolly-pine, *P. tæda;* all products of the southern part of the United States, where the Coniferæ are the principal trees. There are many varieties of the Coniferæ, and all yield gums available for distillation into turpentines and resins.

Turpentine consists chiefly of a hydrocarbon oil ($C_{10}H_{16}$) and a resin called "Colophony" ($C_{20}H_{40}O_2$). Specific gravity, 1.07 to 1.08. It softens at 155° to 175° F. and melts between 194° and 212° F. The spirits of turpentine constitutes about 17 per cent of the yellow pine-tree sap or crude gum. The *Maritime pine* furnishes about 24 per cent of spirits of turpentine.

The exuded gum from all of the turpentine-trees is a yellowish, opaque, tough mass, brittle and crumbly when cold, crystalline in the interior, and of a characteristic taste and odor, a distinguishing feature in all types of the "turpens," designated as the terebinthic odor. The commercial oils of turpentine are as follows:

The German, derived chiefly from the *Pinus sylvestris* (Scotch fir), *P. nigra*, and *P. rotundata.*

The English, from the American or Carolina *Pinus australis* or *P. tæda.*

The French, or Bordeaux, from the *Pinus maritima,* resembles the American turpentine in appearance, odor, and taste, and is considered to be the quickest drier.

The Strasburg is the product from the *Abies pectinata* and from the spruce fir, *Abies excelsa.*

The Venice is the product from the *Terebinthina venita,* or the larch, *Larix europea.*

The Hungarian is from *Pinus pumilio.*

The Carpathian, from the *Pinus cembra,* has a bitter taste.

The Cyprian, Syrian, or Chio, obtained in Chio, is from the *Pistacia terebinthus.*

Templin, or pine-cone oil, is furnished from the cones of the *Pinus pumilio* and the *Abies pectinata.*

The Canadian oil or Canada balsam, from the *Abies balsamea* (Balm of Gilead), furnishes the whitest and purest of all of the turpentines.

Related to the true turpentine-oils are the two volatile oils of the coniferous plants—oil of juniper from the *Juniperus communis,* and the oil of savin from the *Juniperus sabina.*

A characteristic feature in American turpentines is that they polarized to the right, while most of the turpentines from other sources polarize to the left.

The crude resin from which the oil of turpentine is distilled has a specific gravity of 0.95 to 0.98, according to the time of its collection, whether in the first, second, third, or fourth year after the tree is boxed, or during the time of collecting the dried sap in the first flow in the spring, or the summer, or later in the fall. Also its freedom from sand, leaves, bark, and dirt; all of which are readily absorbed by the sticky, drying sap, and are only removed in the process of distilling the gum for spirits of turpentine. Another distillation is required to produce the oil of turpentine or "turps" of the painter.

Fig. 30 shows the old method of boxing the trees to collect the crude resin.

In addition to the exuded gum from living trees, turpentine is also obtained by the distillation of the dead wood from the long-leaf pine-tree when it no longer yields the gum (after the fourth or fifth year), and when it has been turned over to the lumber or cord-wood men. The trees not fit for lumber, or unfavorably located for handling the cord-wood, are cut down and distilled in a kiln or oven similar to that used for the production of charcoal from hard wood.

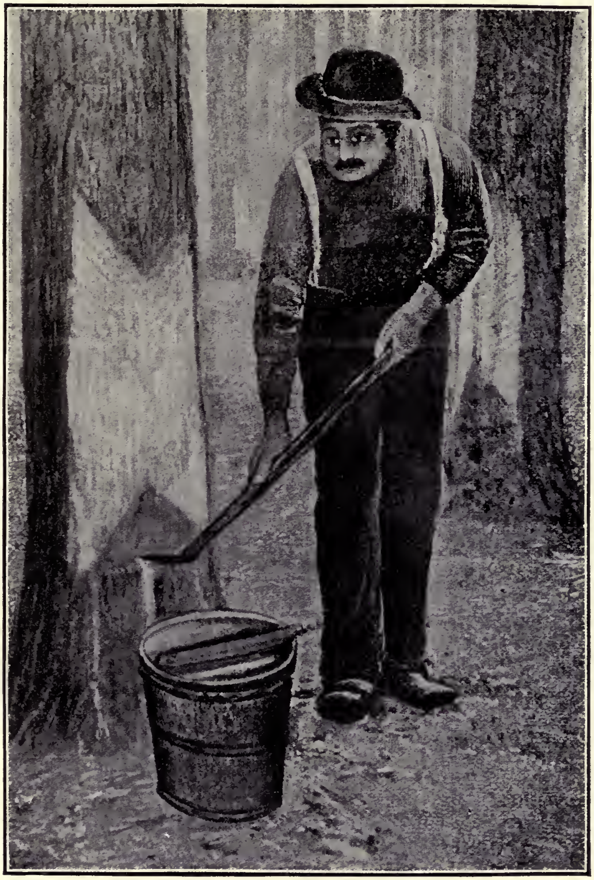

Fig. 30.—Boxing the turpentine-tree.

A cord of fat pine-wood yields by kiln distillation, according to the amount of the pitchy matter in it, whether it is body wood or from the limbs, tops, or decayed wood, the following products:

Turpentine crude oil	22 to 26 gallons	1150 to 1200 pounds.
Pyroligneous acid	86 “ 90 “	
Pine-tar	118 “ 122 “	
Charcoal	54 “ 58 bushels	2200 to 2400 pounds.

Many commercial turpentines contain acid. They are generally the products of kilns, and are not redistilled to free them from the acids. The effect of the use of turpentine in a paint or varnish is to flatten the gloss or lustre.

Even with a pure turpentine not more than 3½ per cent is admissible in a paint; and less than this if the turpentine is poor or fatty.

Pure turpentine-oil is adulterated with crude or undistilled turpentine, light-colored resin-oil, and resin.

These adulterations are detected by the pyroligneous smell and nauseous after-taste on the tongue and by the change in the specific gravity. Also by the reaction produced by adding 8 drops of strong ammonia to 90 c.c. (1.422 cubic inch) to the turpentine. The following are the results:

Pure Oil of Turpentine.	Specific Gravity.	Reactions with Ammonia.
Pure oil of turpentine recently distilled 7.4409 pounds per gal.	0.8678	No effect. The turpentine evaporates quickly. No residuum.
Old pure oil of turpentine 7.4534 pounds per gal.	0.8693	Solidifies in a few seconds, forming a white crystalline substance with the consistency of butter.
Pure turpentine with 10 per cent of resin spirit 7.3496 pounds per gal.	0.8784	Forms an emulsion, which rapidly becomes clear. The ammonia which separates has a pale-yellow color.
Pure turpentine with 10 per cent of undistilled turpentine 7.3496 pounds per gal.	0.8784	Forms an emulsion which becomes clear on standing, gives a semi-transparent sediment of a bluish color, the liquid above being colorless.
Pure turpentine with 10 per cent of resin 7.3686 pounds per gal.	0.8831	Each drop of ammonia appears to solidify as it falls into the oil. On agitation the whole solidifies into a consistent transparent mass.

Characteristics of Oil of Turpentine.

Pure oil of turpentine has the composition of $C_{10} H_{16}$, and at a specific gravity of 0.839 weighs 7 pounds per gallon. At 60° F. the gravity is 31° Baumé, and it weighs 7 pounds per gallon. At 60° F. pure turpentine should weigh not less than 6.802 nor more than 7.278 pounds per gallon.

Benzine at 60° F. has a gravity of 65° to 72° Baumé and weighs 5½ to 6 pounds per gallon. The hydrometer test for benzine is 62°

Baumé. Any benzine or light kerosene-oil added to turpentine will raise the degree to some point between 32° and 65° B. 36° to 38° B. should be the limit of acceptance for turpentine.

Turpentine adulterated with mineral oil will leave a stain on a blotting-paper filter.

An average quality of turpentine boils at 320° to 350° F. and has a flash-point of 103° or 104° F.

Crude turpentine resin boils at 316° F.

Crude turpentine resin, specific gravity 0.98 to 0.95, is dissoluble in water, but readily soluble in ether or spirits of turpentine and in six parts of alcohol. The alcoholic solution has an acid reaction.

Bromine and iodine act violently upon it. When brought into contact with a mixture of nitric and sulphuric acids it takes fire. Turpentine is a solvent of all oils and resinous gums at ordinary temperatures, but some of the fossil resins require a low heat to aid its action.

Adulterants of Turpentine.

Kiln-distilled spirits of turpentine contains pyroligneous and other acids, specific gravity, 0.80 to 0.84.

Crude petroleum, specific gravity, 38° to 48° Baumé; weight, 7.00 to 6.62 pounds per gallon.

Benzine, specific gravity, 54° to 62° B.; weight, 6.39 to 6.10 pounds per gallon.

Naphtha, specific gravity, 62° to 70° B.; weight, 6.09 to 5.79 pounds per gallon.

The pyroligneous acid in turpentine distilled from dead-fat pinewood settles out partially after standing, but commercial brands not redistilled still contain some amount of the acid.

Commercial spirits of turpentine has a specific gravity of 32° Baumé. Any addition of petroleum of 40° B. will be shown by the rise in the hydrometer; each 3 to 5 per cent of petroleum added causes a rise of 1° B. on the scale. If the adulterant is benzine or naphtha, then the difference in the specific gravity is very marked and will at once determine the character of the adulterant, it being much lighter than coal-oil or kerosene.

For the detection of resin in the spirits of turpentine, the polariscope-test is the only one that can be considered strictly accurate, but it is a delicate one, and requires experience to determine results.

A ready method for detecting resin consists in dilute sulphuric acid one part and four parts spirits of turpentine; mix and shake in a test-tube and notice the precipitate, which will be the resin; allow for the resin normal in all turpentines; the pure spirits of turpentine will be found on top of the fluid in the tube. The flash-test for naphtha adulterations consists in heating the turpentine in a double vessel 63° to 65° F. and then flashing it. If it ignites, it is safe to assume the mixture contains more or less naphtha.

The Journal of Chemical Industry, Vol. IX, 1890, p. 657, gives a test for commercial spirits of turpentine, the usual adulterants being naphtha, petroleum, resin-oil, and the inferior Russian oil of turpentine. (See also same *Journal*, pp. 330–557.)

The U. S. Navy Department tests for turpentine are: A single drop placed on white paper should completely evaporate at a temperature of 70° F. without leaving a stain.

A few drops on a piece of white paper, hung vertically before the light, if the turpentine is pure and well distilled, should leave no mark after 5 to 7 minutes. A faint mark indicates the presence of resin due to imperfect distillation. If a gray mark remains for an hour or more, it indicates kerosene or other petroleum oil. If a greasy mark remains over 10 to 12 hours, petroleum is present in large quantities.

It requires from 680,000 to 1,000,000 acres or 1060 to 1560 square miles of forest to supply the turpentine products, whose value is from $8,000,000 to $8,600,000 yearly. Both the export and home demand are increasing from 5 to 8 per cent yearly, and the forest supply for tapping is decreasing in more than an arithmetical ratio of these amounts.

The unit of product for a turpentine crop is 10,000 boxes of 2500 trees from 100 to 300 acres of forest, according to the size of the trees, or an average of 15 trees per acre. When the lumber is exhausted and the cord-wood is cut out, there remains about one-half a cord of wood per tree available for kiln distillation. This will yield about 12 gallons of crude turpentine spirits that would redistill to about 10 gallons of the oil of turpentine per tree. This amount, if it all could be collected and distilled, would yield about 6 times the yearly demand of 22,000,000 gallons. But 95 per cent of this supply of wood would be used for saw-mill fuel, cord-wood, waste, and be unavailable on account of location, or standing as dead-wood forest. The latter is a fruitful source of the forest fires that annually destroy from 3000 to 5000 acres of this valuable timber. Hence but 5 per cent would find its way to the kiln, and furnish about 25,000,000 gallons of turpentine, or a little more than the present (1903) requirement, if the supply came from this source alone.

When the long-leaf pine forests have practically disappeared, they will have to be carefully gleaned once and for all in order to produce a quantity of turpentine equal to the present demand for one year.

A barrel (240 to 260 pounds) of the crude turpentine resin, when distilled, yields from 10 to 11 gallons of turpentine spirits that need to be redistilled to afford a pure oil of turpentine. About one-half or five-eighths of a barrel of resin (170 to 190 pounds) is also a result of this distillation. This resin is redistilled for resin-oils of a number of grades, whose specific gravities range from 0.960 to 0.9910. It also furnishes sixteen recognized grades of commercial resins; those known as W. W. (water-white), W. G. (window glass), are the finest and most valuable, being produced from the first year's run or virgin sap. Each subsequent year of the four or five years that the trees run resin, an inferior quality is produced, that is graded N. (very clear); then M. L. K., J. H. to A., the latter being almost black, and rated commercially as pitch, specific gravity, 1.15.

The flow of resin from the freshly boxed or virgin cut trees is from 250 to 350 barrels of 240 to 260 pounds for the first year, and requires 100 to 200 acres of forest; the flow decreasing to 48 or 60 barrels in the fourth year, that furnishes the poorer grade of crude resin, that contains but little turpentine.

The action of turpentine as a drier for paint or varnish is to form the peroxide of hydrogen from the air that renders them non-drying except upon the surface.

Turpentine, by absorbing oxygen from the air as it stands in the barrel, is liable to become "fatty" ($C_{10}.H_{16}.O_2$) with age, and cannot be properly corrected except by redistilling. The use of such turpentine in a paint is to render it "tacky." Painters resort to the use of benzine to correct this fatty condition, but it is detrimental to the life of the paint and to its gloss.

Fatty turpentine evaporates slowly on blotting-paper and leaves a stain upon it.

A drop of turpentine allowed to spread itself slowly down a piece of glass coated black upon the other side of the plate will show a bluish tinge at the edges if petroleum is present even to the amount of 5 per cent.

Adulterations of turpentine with resin-oil are shown where the residue left after evaporating a small quantity in a saucer is of a sticky nature and resinous odor after it is ignited.

The use of tank-cars that have been used to transport crude petroleum is responsible for a great deal of the impure oil of turpentine. The crude oil of turpentine thus transported and carelessly redistilled will carry over enough of the petroleum to sensibly raise the specific gravity of the turpentine.

From a large number of tests of commercial turpentines by various State associations of painters, and by individual painters and experimenters, the general result appears to be that 50 per cent of the samples showed adulterations ranging from 5 to 20 per cent. There are no penalties for the adulteration of either turpentine- or linseed-oil, and when adulterations are present in any form or amount, generally, the detection of them is beyond the power of the ordinary purchasing agent or painter.

The Secretary of Agriculture for the United States for the year 1890 reports that at the present rate of consumption, the forests of the long-leaf or turpentine pine will be exhausted in from 8 to 10 years. Practically the yellow-pine forests of North and South Carolina are exhausted, and the production of turpentine and resin is now centred in Georgia, Alabama, and Florida. The belt of long-leaf pine timber extends about 150 miles inland from the seacoast across the above States to the Mississippi River. Texas has been comparatively denuded of the yellow pine.

Where the supply of turpentine and resin will come from when these forests are extinct, is an unsolved problem. The second growth of timber following the pine appears to tend toward the scrub-oaks and non-resinous trees—cedars, etc.

Fig. 31 shows the modern or improved method of scarfing the turpentine-tree and collecting the sap, as distinguished from boxing the tree.

Over 75 per cent of the turpentine produced in the United States is exported. Europe has no yellow-leaf pine forests that furnish any great amount of turpentine. Norway, Sweden, and Russia furnish resins from the other pine varieties of the Coniferæ, but they rate low in the amount of turpentine they contain as compared with the American or hot-belt growth of the long-leaf yellow pine.

The exports of spirits of turpentine of all grades from the United

States for the year 1897, to only six of the European countries, were as follows:

Austria	65,000	gallons.
Belgium	2,098,810	"
Germany	2,418,790	"
Italy	398,710	"
Netherlands	2,359,590	"
Great Britain	8,476,700	"
Total	15,817,600	"
Other countries	682,400	"
	16,500,000	"
United States consumption	5,500,000	"
Total production	22,000,000	" of turpentine, and
	1,600,000	barrels of resin— 350 to 400 pounds per barrel.

Fig. 31.—Boxing the turpentine-tree. New method.

Mr. F. G. Frankorter* reports "that the products of the pitch made from the butt of the Douglas fir or Oregon pine are unusually

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* "Science," July 24, 1903. *American Chemical Society Journal*, 1903

rich in pitch. They contain as high as 41.6 per cent, of which 21 per cent is turpentine. The latter has about the same boiling-point (150° F.) as that from the northern pine, but differs from it in other properties. The kiln products (turpentine, pyroligneous acid, charcoal, pitch, etc.) from one butt discarded as unfit for lumber had a value of $275." The tree grows on any mountainous soil where the spruce, hemlock, or any Coniferæ grow, and may be hereafter utilized for its turpentine-supply only. It grows from British Columbia to Mexico in large forests, the trees often reaching 300 feet in height. The bark is useful for tanning.

CHAPTER XX.

CARBON BISULPHIDE

(CARBON DISULPHIDE—SULPHO-CARBONIC ACIDS).

THIS carbonic anhydride (CS_2) has a specific gravity at 32° F. of 1.027 to 1.072. At 60° F., 1.272 or 10.6135 pounds per gallon. The specific gravity of *its vapor* at 60° F. is 2.6292 to 2.644. The boiling-point of the commercial article is 118.4° F., that of the refined 109.4° F.

It is composed of 15.8 per cent of carbon and 84.2 per cent of sulphur (CS_2), and is produced by passing the vapor of burning sulphur (sulphurous-acid gas, SO_2) over charcoal kept at a red heat. This is the commercial method of manufacture. It is highly inflammable; its vapor mixed with air takes fire at about 300° F. and explodes with great violence. It is a colorless, heavy, very volatile liquid, possessing an acid, pungent taste and a very fetid alliaceous odor, due to the impurities of 8 to 10 per cent of sulphur and hydrogen compounds in the unrefined product. When refined, it loses the nauseous smell and has an ether-like odor, but it is necessary to keep it under water in air-tight iron vessels.

Carbon and sulphur do not combine when simply heated together in the solid state, because the sulphur volatilizes before the necessary heat is attained. But when the charcoal is ignited to redness and the sulphur vapor is passed over it, CS_2 is formed.

Carbon bisulphide is deadly poisonous; inhalation of even very dilute vapor producing giddiness and vomiting, with irresistible fits of weeping, violent pains in the legs, and a collapse of all the bodily and mental powers; paralysis, idiocy, and death. Five per cent of the vapor in any confined space ensures the death of all larvæ, smaller mammalia, birds, and reptiles. A solution of ferro-carbonate in carbonic-acid water is a partial remedy for the symptoms on first attack.

It is a solvent of all fats, oils, resins, india-rubber, phosphorus, bromine, chlorine, iodine, camphor, etc., and mixes in almost all proportions with alcohol, ether, benzine, and all the fixed and volatile oils.

It is used to extract the oil from seeds, particularly linseed, which is heated and pressed to remove some of the oil before being submitted to the action of the bisulphide. The residue cake contains only 2 per cent of oil and about 7 per cent of water, while the cake from the ordinary process of manufacturing linseed-oil from the steamed linseed contains 9 per cent of oil and nearly 15 per cent of water. The oil so expressed is of good color, but contains more mucilage and less of the glyceride element.

The loss in the manufacture of the bisulphide is about 50 per cent of the charcoal and 17 to 18 per cent of the sulphur.

The use of the bisulphide of carbon for a paint vehicle is more for the cheaper grades of roofing or color paints and for wooden structures of minor importance than for the better grade of house or ferric paints, though in many of the latter it is used freely, judging from the odor. Its use is simply as an adulterant of the oil and to cause a quick drying of the paint, and wherever used it may be considered to accompany a cheap oil, and the grade of the pigments mixed with it will in general be as low as the vehicle.

Like benzine driers, it sensibly lowers the temperature of the surface of the body being covered, and in cool or damp locations this reduction is often enough to reach the dew-point and cause a sweat-deposit on the surface of the paint, causing it to peel.

There are special grades of carbon-blacks, or bisulphide-of-carbon paints, under many trade-marks, specially noted in trade literature for their excellence as coatings for brine, ammonia, refrigerating and brewers' tanks and barrels. In some of these the paint appears to give good results. Nearly all of these paints are simply asphalt or natural bitumen, refined more or less, and a bisulphide-of-carbon vehicle containing little if any linseed-oil. They evaporate quickly and leave the bitumen coating behind, and probably coat the surface more thoroughly than is possible to apply bitumen hot or in any other manner.

For painting galvanized iron, the bisulphide of carbon appears to be of merit; at least the coatings containing some amount of bisulphide either as the principal vehicle or as a drier do not peel as readily as oil paints of similar color and pigments. This favorable point is more marked in the case of the brownish-black or full-black paints, and is probably due to the bisulphide element dissolving the greasy coating of the sal-ammoniac soap, that forms on the surface of the galvanized sheet in the process of galvanizing. The presence of this soapy coating prevents the oil-paint coating from bonding to the metal, and it dries as a loose skin, peels easily, sometimes before it is dry.

The bisulphide being a solvent of all semi-glutinous substances loosens up this soap and incorporates it into the mass of the coating, and the quick evaporation of the bisulphide leaves it there.

There are many instances on record of the disastrous results upon the health of the painters who spread bisulphide-of-carbon mixtures. A noted one is its use with maltha (a mineral bitumen) for the internal and external coatings of a number of miles of steel-riveted water-pipe mains, where the application of this mixture was attended by the disability, insanity, and death of a number of the painters. Its use as an anti-corrosive coating for protecting miles of water-pipes was wholly experimental, without a single record on which to base such an application of an untried material, and especially one known to be decidedly inferior and uncertain for minor purposes. Had a gill of this maltha paint been spread in a room where the Board of Water Commissioners and their Engineering Staff held council over the protection of water-pipes from underground corrosion, all the subsequent injury to the painters and expense of application and removal could have been avoided. Another coating was substituted for the maltha, but not before a number of miles of the water-mains had been laid and covered in with no better protection against corrosion than that which could have been had with a coating of boiled skimmed-milk glue.

In the open air bisulphide mixtures can be spread without material danger or discomfort to the painters, but they have not a single element of protective value that warrants their application to any ferric structure of magnitude. They should only be spread on those of minor character, where the corrosion or decay is of no material importance, and the question of the cost of the coating and its temporary appearance governs.

Frequent analyses of bisulphide paints show about 50 per cent of a low-grade resin, bitumen, and lampblack, for the pigment, with barytes or silica added to give weight. Bisulphide-of-carbon coatings brush out easily and spread over a large area, as the vehicle is very thin compared with that of a linseed-oil paint. This feature of itself is against their protective quality. In such cases the pigments are but thinly covered or embedded in the vehicle, the quick drying of which by evaporation leaves a porous, crumbly mass with hardly any bond between the atoms of the pigment or to the covered surface. The dried coating soon shrinks in mass, cracks finely, is easily rubbed off by the hand, and requires to be wholly removed before repainting, even to apply another coating of the same compound.

Analyses of dried bisulphide-of-carbon coatings show from 5 to 10 per cent of sulphur, certainly not a suitable substance to recoat with any linseed-oil paint, unless the prompt peeling of it is desired. For ferric coatings, sulphur in any form or amount either in the pigment or vehicle is to be avoided.

A new process for the manufacture of carbon bisulphide by an electric furnace has lately been developed and patented in the United States by Edward R. Taylor, of Penn Yan, N. Y.* Whether the new process will supersede the old or burning-charcoal process remains to be commercially demonstrated. Its many uses in the arts outside of paints will always cause it to be in demand. Its present price of 4 to 4½ cents per pound, equal to 42 to 45 cents per gallon, leaves nothing to recommend it as a substitute solvent or drier for turpentine in a paint.

A French chemist, M. La Roy, has suggested an improvement in bisulphide of carbon as a substitute for turpentine in paints and varnishes. It is the chloride of carbon, or more particularly, the tetrachloride of carbon, CCl_4. Its characteristics compared with turpentine are interesting. It is a colorless, limpid fluid, *specific gravity,* 1.56 or 13 pounds per gallon; boils at 170° F., being more volatile than turpentine, having an aromatic, pungent odor, is soluble in alcohol and ether, and dissoluble in water. The fluid is *not inflammable,* and dries quicker than turpentine. It can be mixed in all proportions with all of the usual paint solvents, including the bisulphide of carbon. Varnishes made from it are exceptionally hard and brilliant.

In comparison, turpentine ($C_{10}H_{16}$) has a specific gravity of 0.86 to 0.88=7.176 to 7.343 pounds per gallon, boils at 160° F., and is quite inflammable both in fluid or vapor. The tetrachloride flattens the gloss in oil paints the same as turpentine, but adds weight to the paint.

Tetrachloride of carbon † is produced: First, by the action of

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* "Carbon Bisulphide in the Electrical Furnace." Described in the *Electrical World and Engineer,* also in the *American Gas Light Journal* (N. Y.), Jan. 6, 1902, p. 11. Illustrated.

† Watts's Dictionary of Chemistry, Vol. I, p. 765.

chlorine on marsh-gas. Second, by the action of chlorine on chloroform exposed to the sunlight. Third, the probable commercial process of manufacture, by the action of chlorine on the disulphide of carbon; the reaction being, $CS_2+4Cl_2=CCl_4+2SCl_2$. Chlorine, saturated with the vapor of the sulphide of carbon by passing it through the liquid, is passed through a red-hot tube or retort filled with pieces of porcelain, the outlet of the retort being connected to a receiver packed in ice. The condensed yellow mixture of tetrachloride of carbon and chloride of sulphur thereby obtained is slowly added to an excess of potash lye or milk of lime, the mixture being agitated from time to time and afterward distilled. The tetrachloride of carbon passes over, mixed with some of the sulphide of carbon. If too much of the sulphide has been mixed with the chlorine, or if the decomposing heat has not been strong enough, the sulphide of carbon can be removed by leaving it for some time in contact with the potash lye.

No estimated cost of the tetrachloride product is at present given, but its field of usefulness in the manufacture of paints and varnishes, also as a special drier, is favorably indicated from the few trials and experiments thus far had with it.

CHAPTER XXI.

JAPAN DRIERS.

Japan driers or japans vary greatly in their composition and are very erratic in their action as drying agents. Specimens from the same manufacturer, taken from stock at different times, are widely different in drying qualities, while any attempt to classify the japans of different manufacturers is one of the vexations of the master painters. Probably a good rule for painters to follow in the case of japans is, when one has been found to suit them, to lay aside a sample of it to compare with all future supplies, and to stick to that manufacturer and brand just as long as it comes up to the mark.

The general composition and process of manufacture of japans are: Gum shellac is cooked with linseed-oil in a varnish kettle until it becomes thick and partakes of the nature of a varnish. Litharge and other substances are added to quicken the drying of the resulting product. When the mass has cooked down to a thick substance called a "pill," it is allowed to cool and then thinned down with turpentine. Japan is a light-colored brownish-yellow liquid of about the consistency of varnish. A thin surface of it dries in from 15 to 20 minutes. The care exercised in the manufacturing process and the purity of all the materials used, affect its quality, and are the cause of such erratic results from its use.

The reputation of a japan or varnish manufacturer counts for much, but it does not always ensure a good article, if the price governs the selection.

Formulæ for japans are numerous and are trade secrets. The following are representative samples:

One gallon cold-pressed old linseed-oil, $\frac{3}{4}$ pound of D. C. or L. C. gum shellac, $\frac{1}{2}$ pound gold litharge, $\frac{1}{2}$ pound burnt umber, $\frac{1}{2}$ pound of red lead, 6 ounces sugar of lead. Boil together with constant stirring for 4 hours, or until all of the ingredients are dissolved. Remove from the fire, and when cool add 1 gallon oil of turpentine; stir well while it is being added.

A cheap japan: Mix 4 gallons pure linseed-oil, 4 pounds each of litharge and red lead, 2 pounds of powdered *raw* umber. Boil slowly for 2 hours and add by degrees 7½ pounds D. C. gum shellac, and boil ½ hour longer or until the ingredients are well mixed. Add by degrees 1 pound powdered sulphate of zinc, and when nearly cold, stir in 7 gallons of spirits of turpentine.

The "Bung-hole Drier" formulæ are as numerous as the oil compounders. The following represent a few of the compounds used:

LEAD OILS.

Linseed- or nut-oil	1 gallon.
Litharge	1 pound.

Linseed- or nut-oil	1 gallon.
Litharge	½ pound.
Sugar of lead	½ pound.

MANGANESE OILS.

Linseed-oil	1 gallon.
Potassium permanganate,	100 grains.

Linseed-oil	1 gallon.
Pure hydrated protoxide of manganese	½ ounce.

MANGANESE AND LEAD OILS.

Linseed-oil	1 gallon
Umber	5 ounces.
Gold litharge	5 ounces.
Red lead	5 ounces.

Linseed-oil	1 gallon.
Borate of manganese	1 ounce.
Acetate of lead	1 ounce.

Linseed-oil	1 gallon.
Permanganate of potash	4 ounces.
Acetate of lead	4 ounces.

Linseed-oil	1 gallon.
Manganese protoxide hydrate	1 ounce.
Red lead or litharge	1 ounce.

See also Boiling Oil, Chapter XXIII. For the effect of different driers upon linseed-oil, see Thorp's experiments, same chapter.

The following is an extract from a Report of "Test on Liquid Driers," read at the Sixth Annual Convention of the Master Painters and Decorators' Association of the United States, held in Detroit, Mich., on Feb. 11, 12, and 13, 1890.

	Raw Linseed-oil Dries in		White Lead Dries in		Vandyke Brown Dries in		Lamp-black Dries in	
	Hrs.	Min.	Hrs.	Min.	Hrs.	Min.	Hrs.	Min.
1 part Azote drier (trade-mark) to 1 part	1	50	1	50	2	15	1	50
" " " " " " 5 parts	2	35	2	50	4	20	2	20
" " " " " " 10 parts	3	40	3	50	6	15	3	45
" " " " " " 15 parts	4	30	5	00	9	40	6	20

Brown japan should mix well with raw linseed-oil in any proportion up to 15 per cent, and should stay mixed for at least 6 hours without showing sediment or separation, called "curdling."

When applied in a thin film to a clean, dry piece of glass placed in a vertical position, the japan should be dry to the touch in about 2 hours, and should dry hard without becoming brittle in 6 hours.

The so-called concentrated driers are made by heating linseed-oil with lead and manganese salts or oxides in excess, until the product becomes viscous, like a sticking-plaster or birdlime. Liquid driers are concentrated driers, thinned out while hot with naphtha or spirits of turpentine. When applied in a thin film to glass and placed in a vertical position, they should be dry to the touch in 2 hours, and harden in about 8 hours. After 48 hours the drier should not rub off in the form of a fine powder when the finger is rubbed briskly over the surface. Liquid driers should mix freely with raw or boiled linseed-oil, turpentine, or benzine in any proportion without showing clots or precipitate after standing 48 hours in the open air.

Inferior liquid driers can be recognized by the odor of benzine when the sample is slightly warmed; by the powdering of the hardened film when rubbed by the finger, and by the rapid evaporation when exposed to the air, with consequent separation of the ingredients.

The quality of a japan depends as much upon its cooking as upon the quality and kind of the materials in its composition. Too high a heat or too long exposure to the heat frequently spoils it.

Gum is added by some manufacturers of japans to harden the oil. This, while causing the japan itself to dry more rapidly, reduces its power to dry an oil paint. Gum is a very uncertain substance in the formula of japan manufacturers. It may mean the spruce cud of the schoolgirl, common resin, or the best grade of the fossil resins, over thirty in number, with many varieties in each number.

CHAPTER XXII.

FLAX-PLANT AND LINSEED.

LINSEED is the seed product of the *Linum usitatissimum*. This plant is a native of India or Eastern Asia, and its cultivation has existed from the earliest ages, distinct evidences of its existence during the Stone Age being preserved to the present day in the rough and worked flax made into bundles, found in the lake dwellings of Switzerland.

It is mentioned in the book of Exodus as one of the products of Egypt in the time of the Pharaohs. Among the plagues of Egypt, that of hail destroyed the flax and barley crops, "for the barley was in the ear and the flax was bolled" (Exodus ix. 31).

Pharaoh "arrayed Joseph in vestures of fine linen" (Genesis xli. 42).

Solomon purchased linen yarn in Egypt and Herodotus speaks of the great flax trade of Egypt.

Numerous pictorial representations of the cultivation and preparation of flax are sculptured on the walls and tombs of Thebes, showing the varieties of flax in the red and white flower, the manner of pulling, retting, and hachelling as practised when Jacob dwelt in the land of Goshen; and, except in some minor particulars, or in certain favored locations, are precisely the same as practised at the present day.

The crushing of the seed in a mortar, grinding it on a stone slab by a muller, the pressing out of the oil with stones, the seed-bag, the burning lamp showing that the ancients knew the value of heat to aid in the extraction of the oil, and the painter with his bristle brush and paint-pot is also delineated.

Flax is more extensively and successfully cultivated in Belgium than in any other part of Europe, that raised in East and West Flanders (the Coutrai flax) being the most valuable of the world's crop of this fibre. It is used in the manufacture of Brussels lace. The crop often exceeds in value the land on which it is raised, bringing

$500 to $750 per ton, while the ordinary fibre crop brings $200 to $400.

Prof. Hodge's (of Belfast) experiments with 7770 pounds of dried flax yielded the following results:

1946 pounds of bolls, which furnished 910 pounds of seed. The 5824 pounds (52 per cent) of flax fibre, lost in steeping 1456 pounds, leaving 4368 pounds of retted stalks, and from that 702 pounds of finished fibre were produced. The weight of fibre was equal to about 9 per cent of the dried flax stalk with the seed-bolls, 12 per cent of the bolted straw, and over 16 per cent of the retted straw.

Fig. 32.—Jerusalem flax-plant blossom. It grows wild in Palestine, covering large areas around Jerusalem. (Blue flower.)

By Schenck's (American) method, 100 tons of the dried flax straw gave 33 tons of bolls with 27.5 tons' loss in steeping; 32.13 tons were separated in scrutchings, leaving 5.9 tons of finished fibre and 1.47 ton of tow and pluckings.

Generally two bushels of linseed are sown per acre, and the yield in finished fibre is from 600 to 800 pounds, the market price of which is about 12 cents per pound. The yield of seed is from 8 to 10 bushels of 52 pounds, and is graded and classified as to quality and condition as closely as any of the grains. The crop is very exhausting to the soil; potash and phosphoric acid are the chief ingredients that the soil requires to produce a good crop of either the fibre or seed. It requires from 400 to 600 pounds of mineral or phosphate fertilizers per acre, beside barnyard and other manures, to keep the soil in condition, and then only two or three crops can be raised in succession, when other crops must be substituted for from 5 to 8 years.

New England formerly raised large quantities of flax for the fibre, but the advent of cotton manufacture soon displaced flax culture, and this, with the exhaustion of the soil and absence of phosphate fertilizers, caused an abandonment of the flax crop in that part of the United States, early in the past century.

America furnishes about one-fourth of the world's supply of linseed-oil. The crop of linseed for the years 1900–1901 was from 16,000,000 to 17,000,000 bushels. The average yield of oil was 18¾ pounds of oil per bushel, or 2.465 gallons of 7½-pound oil; equal to 40,000,000 to 42,000,000 gallons. In general, the American crop is comparatively free from the adulteration of the wild mustard and other acrid seeds that render the oil-cake almost valueless for a cattle food. Though, in this respect, it is better than most of the foreign seeds, it is, however, the practice for many seed-crushers to add the screenings from the linseed and grain elevators to their linseed in the crushers, and this not only furnishes a bitter oil-cake but a poorer oil.

The American linseed crop is now chiefly produced by the Northwestern States, where the rich prairie soil is favorable for a heavy seed crop without much fertilization. The fibre in these States, from its distance to market and the difficulty of preparing it, is of minor importance, and the plant is generally allowed to fully ripen before harvesting, the flax being burned, like the straw from the wheat-fields, to get rid of it. Duluth and Chicago are the commercial centres for the distribution of the Western linseed crop, the yearly production of which is not clearly determined at this date (February, 1902) owing to the incomplete state of the last United States Census.

The Argentine Republic is the greatest flax-growing country in the world. Flax-growing was begun in Argentina nearly a hundred years ago, but not until about 20 years back was any attempt made to raise it to the proportions of a national industry. In 1881 some 67,000 acres were planted in flax in the province of Buenos Ayres. The success of the venture led to wider planting in that province,

FIG. 33.—Flax-plant—flower, seed-vessel, and seed.

Its flower is blue. Fig. 1 represents a flower leaf or petal; there are five to each flower, which is of a very regular and perfect kind, having five petals, five pistils, five stamens, five sepals. Figs. 2 and 3 are sepals, or cup leaves, to the flower; Figs. 4 and 5 represent the seed-vessel, with its tall stamens and taller pistils; Fig. 6 is a stamen; Fig. 7 is a seed-vessel cut open, showing ten seeds. The stamens fertilize the pistils, the pollen falling upon the top of the pistil, or probably carried there by some busy bee. Within each of the pistils (not to speak exactly) grow two seeds, as seen in Fig. 7, divided by a little wall. Fig. 8 is a ripe seed-vessel. Sections of the seed and the perfect seed are seen in Figs. 9, 10, 11, and 12.

and in Cordova, Entre Rios, and Santa Fé. To-day the crop is one of the most important in the country, and surpasses in magnitude that of any other land.

The plant is grown only for the seed, and as soon as the latter is secured the straw is burned. An average of 1000 pounds of seed is raised on an acre, and in some cases the yield is 2000 pounds. The export of flaxseed from the four provinces named amounts to 500,000 tons a year, which is one-half the entire product of the world and equals 54,200,000 gallons of oil. Not more than 20,000 tons are retained for domestic use, and there appear to be no linseed-oil mills in the country, as all the oil used there is imported. One wonders what the effect upon the markets of the world might be if Argentina should export linseed-oil and cake instead of raw flaxseed, and could transform the straw into linen thread and cloth instead of burning it.

Ireland, England, Belgium, and Central Europe raise the best flax for fabric purposes, but seeds gathered from these sources being unripe, furnish poor, watery oil.

Russia has a large acreage of flax for seed purposes and furnishes about one-sixth of the world's supply of linseed, the yield being about 8 bushels of 56 pounds to the acre; the flax fibre is of minor importance, being woody and subject to great waste in preparing it for fabric.

Russian seed is exported for seed purposes as well as for oil extraction. In Russia hempseed is sown with the flaxseed, and comprises nearly one-tenth of the seed crop, but as this seed furnishes a siccative oil, it is not an objectionable adulterant, such as the seeds from the rape, colza, mustard, and many other non-drying oil-seeds, called "flax-dodders." The adulteration from these acrid seeds is so great that the waste product in the form of oil-cake, formerly a valuable cattle food, is now so strongly impregnated with the biting taste of these seeds, that cattle refuse to eat it, and it is now used for fuel or fertilizing purposes.

India furnishes about one-eighth of the world's supply of linseed. It is grown as a mixed crop for the seed only. The India flax-plant has been deteriorating for over 200 years, until it is now an inferior shrub from 12 to 16 inches high. The climate is favorable for the oil-producing quality of the seed. The white-flower plant produces about 2 per cent more oil than the blue-flower variety, also a sweeter and softer oil-cake. The edges of fields devoted to other crops are sown with linseed for seed purposes, which is allowed to fully mature before gathering, the ordinary linseed crop being harvested just before the seed has fully matured, and while it contains more water than if fully ripened.

Rape-seed is sown in large quantities with the linseed. Its yield of seed and oil is very large, and when refined it passes as colza-oil from coleseed. These seed-oils are used for burning, lubrication, and in the manufacture of india-rubber articles, because of their non-drying qualities. India is very prolific in oil-bearing seeds; the mustard and many other acrid seeds grow wild, are very rich in oil, and all are freely used to adulterate linseed to an admitted amount of 10 per cent and possibly 15 per cent more.

The quality of the flax, also of the seed, varies quite as much as any crop of grain or vegetables, according to the locality in which they are raised, the soil, weather, and other influences affecting the fibre or oil, and the crop is quite as exhaustive to the soil as wheat or corn.

Samples of linseed grown in various parts of the world and averaged from a collection of ripe seeds weighed from 48 to 52 pounds per bushel, and the yield of oil was quite as variable, viz.:

GALLONS OF 7½-POUND OIL PER 112 POUNDS OF SEED.

Best Odessa seed	15	to	16	gallons.
Archangel "	18	"	19	"
Good commercial seed	15.5	"	16	"
East Indian seed	17	"	16.5	"
Sicilian "	16	"	16.5	"
General results by a large crusher for all seeds	14	"	17	"

American seed, 52¼ pounds per bushel, gave 26.55 per cent of oil, or 13.87 pounds.

Linseed in its dry state, as analyzed by Dr. Ure, contains:

Oil	11.265	per cent.
Wax	0.146	" "
Soft resin	2.488	" "
Resinous coloring matter	0.550	" "
Yellowish coloring matter analagous to tannin	0.926	" "
Gum	6.154	" "
Vegetable mucilage	15.12	" "
Starch	1.48	" "
Gluten	2.932	" "
Albumin	2.782	" "
Saccharine extractive	10.884	" "
Enveloping material, including some vegetable mucilage	44.382	" "
	99.109	" "
Other substances and loss	.891	includ-

ing free acetic acid, some acetate, sulphate, and muriate of potash, phosphate and sulphate of lime, phosphate of magnesia and silica.

Analyses of linseed by Meurein (*Journal of Pharmacy* [3], XX, 96):

Gum and soluble salts	14 per cent	Episperm. 21 per cent.
Soft resin and fixed oil	1 “ “	
Matter insoluble in water but soluble in ether	4 “ “	
Water	2 “ “	
Soft resin and fixed oil	6 “ “	Endosperm. 23 per cent.
Matter insoluble in water but soluble in ether	12 “ “	
Matter soluble in water	3 “ “	
Water	2 “ “	
Fixed oil	30 “ “	56 per cent.
Matter insoluble in water but soluble in ether	18 “ “	
Matter soluble in water	3 “ “	
Water	5 “ “	
		100 per cent.

Analyses by Anderson:*

Albuminous substances	24.44 per cent	100 per cent.
Gum and cellulose	30.73 “ “	
Oil	34.00 “ “	
Ash	3.33 “ “	
Water	7.50 “ “	

Way's analyses of 33 samples of linseed from various countries:

Nitrogen	3.3	to	5.28	per cent.
Fat	34.70	“	38.42	“ “
Ash	2.68	“	5.64	“ “
Water	8.51	“	12.33	“ “

Way's analyses, ditto of the oil-cake from above samples:

Nitrogen	3.92	to	5.25	per cent.
Fat	6.60	“	15.32	“ “
Ash	5.45	“	22.66	“ “
Water	6.56	“	10.26	“ “
Albuminous substances	25.00	“	36.00	“ “

The general composition of all siccative oils is:

Carbon	77.40	to	76.00	per cent	Konig.
Hydrogen	11.30	“	11.10	“ “	
Oxygen	12.70	“	11.50	“ “	

Linseed † also contains a large quantity of mucilage deposited in the outer layers of cells of the epidermis, which swells up on macerating

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* “Analyses of Linseed.” *Highland Agricultural Society Journal* (New Series), Number 69, p. 376.

† Schmidt. *Amer. Chem. Phar.*, II, 26.

the seed with water, sufficient to burst the cells. One part of linseed boiled in 16 parts of water yields mucilage enough to be drawn out into threads, and forms a dark-colored spongy mass when dry. This crude mucilage contains in addition to the true vegetable mucilage, legumin, albumin, and an organic acid, probably malic acid; also ash constituents, chiefly lime, potash, and iron, partly as phosphates, and partly united in the ash by carbonic acid. Linseed mucilage precipitated by alcohol gives 11 per cent of ash containing 4 per cent of carbonic acid.

Linseed-oil has a specific gravity of 0.928 to 0.953, or 7.743 to 7.952 pounds per United States gallon. The oil from an average quality of ripe seed extracted by various processes contains:

	Cold Process.		Hot Process.
Carbon	75.17 per cent.	Carbon	78.11 per cent.
Hydrogen	10.98 " "	Hydrogen	10.96 " "
Oxygen	13.85 " "	Oxygen	10.93 " "
	100.00 " "		100.00 " "

The carbon-disulphide process gives more oxygen and less carbon. The oil extracted by the naphtha and percolating process does not show any material difference in the quantity of the oil, but is thought to give a quicker drying oil than by the old or cold-drawn process. But, however, it leaves some of the glucerides of the oil in the oil-cake as well as some of the albumin.

The glucerine in the oil in the form of gluceride or other ethers is needed in the change of the fatty acids to form the soap compounds that give the binding quality to the oil. The albuminous substances are organic and are subject to decomposition, and constitute "the drops" or "mucosities" that the boiling process removes, or if the oil is used in its raw state, the driers added are intended to affect them so that they may be oxidized and dried.

Unripe linseed or the seed from flax raised for the fibre (the condition that furnishes a large part of the commercial linseed-oil) contains 5 to 8 per cent of water.

The yield of oil from the different classes (red, blue, or white flower) of linseed varies from 20 to 33 per cent of the weight of the dry seed. The classification of American linseed, in regard to its quality, is established by the Board of Trade of the city of Chicago, as follows:

No. 1. The minimum weight per bushel shall be 51 pounds, the maximum quantity of field-stock, storage, or other damaged seed not to exceed 12½ per cent.

No. 2. The weight per bushel shall be 50 pounds, the damaged seed not to exceed 25 per cent.

No. 3. The weight to be not less than 46½ pounds per bushel; the damaged seed, not to be in excess of 20 per cent, is graded "Rejected."

No. 4. No grade. Seed comprises all damp, mouldy, warm seed or those in a heated condition and unfit for temporary storage. All seed that is burnt, smoky, or intermixed with burnt seed is posted as "Burnt or Smoky Flaxseed."

All sales of flaxseed are made upon the basis of *pure seed;* that is, seed tendered for contract deliveries may carry impure, damaged, or foreign seed matter, but *must contain the sale-quantity of pure seed as given,* and for such pure seed only shall payment be required.

Linseed yields by the

Cold process of extraction,	about	20	per	cent	of	oil.
Hot process " "	"	27	"	"	"	"
Carbon-disulphide process,	"	33	"	"	"	"

Or from 15 to 18 pounds of oil per bushel of No. 1 commercial linseed by the most improved processes of extraction.

The average results in oil of a number of samples of the following substances, extracted by filtration in 100 parts, are as follows:

Linseed............	27.15 per cent.	Walnuts...........	50.06 per cent.
Hemp-seed.........	25.87 " "	Almonds..........	52.41 " "
Poppy-seed........	49.40 " "	Grape seeds........	17.95 " "

Linseed-oil corresponds to the formula (Mulder) $C_{16}H_{25}O_2$ or $C_{32}H_{.4}O_3$. It is an hydride of linoleic acid ($C_{16}H_{26}O_2$). *Specific gravity,* 0.9266. Linoleic acid is a faint-yellow, limpid oil, insoluble in water, and does not solidify at 18° F., and has both the nature of an oil and a resin. It decreases continually in weight for 90 days, losing from 5 to 8 per cent.

Linoleic acid is peculiar to all siccative or natural-drying oils, and when fully oxidized by exposure to the air, forms oxylinoleic acid ($C_{32}H_{54}O_5$) or linoxyn (Mulder).

Hazura and Bower (*Monatsch.*, Vol. I, p. 459) found that the rate of oxidation and consequent hardening of linseed and other siccative oils depended upon the ratio of linoleic and linolenic acids present.

The linoxyn formed is insoluble in water, dilute acids, alcohol, or ether, and is heavier than water.

Hazura describes linseed-oil as formed of linolic, linoleic, and iso-linolenic acids, and that a high proportion of the two latter acids is characteristic of this oil.

Linseed-oil is composed of drying oil, 80 parts, and non-drying or fatty oils, 20 parts. Of the latter, 8 parts are glycerine ether, the volatile element of the oil, that in the chemical changes among the oil acids by the absorption of oxygen in the process of drying, is absorbed or lost in the change to linoleic acid, with a direct loss in weight of the new oil compound.

The fatty acids in linseed-oil are:

Margaric acid	$C_{17}H_{34}O_2$;	specific gravity	0.810
Palmitic or benic acid	$C_{16}H_{32}O_2$	" "	0.809
Oleic acid	$C_{18}H_{34}O_2$	" "	0.808
Stearic acid	$C_{18}H_{30}O_2$	" "	0.805

Margaric acid is considered simply as a mixture of stearic and palmitic or benic acid of identical composition ($C_{18}H_{34}O_2$).

The composition and specific gravities of all the fatty oils vary but little, and the influences that affect one affect all.

Oleic ether ($C_{20}H_{32}O_2$), *specific gravity*, 0.807, associated with the fatty acids, dissolves all solid fats, stearic, palmitic acids, etc.

The glycerides or glycerine ethers have the characteristics of ethylin ($C_3H_{12}O_2$); they are the most volatile of the group, and form a component part of the fatty elements in all siccative oils. The heavy odor recognized when a burning tallow candle is blown out is due to the glycerine ether that comes from the smoldering wick. A heat of 170° F. is adequate to dispel or to cause an absorption of the glycerides into the fatty acids in the oil to form the insoluble soap compound. The albuminous substances in the oil coagulate at about 160° F., and in the steamed or hot process of extracting linseed-oil, the meal is cooked at 190° to 200° F. to prevent the albumin from flowing out when pressed.

These changes indicate the merits of a low and long-continued heat in the process of boiling oil, instead of the quicker and more energetic changes due to higher temperature of the oil, and will be referred to hereafter.

The siccative oils of commercial importance are 20 in number, the principal of which are linseed, poppy, hemp, walnut, sunflower, grape, Scotch and silver fir, and spruce. The specific gravities of the whole number (20) range from 0.9202 to 0.9358, varying so little that the hydrometer-test is of little moment to determine their character. The vegetable non-siccative oils of commercial importance

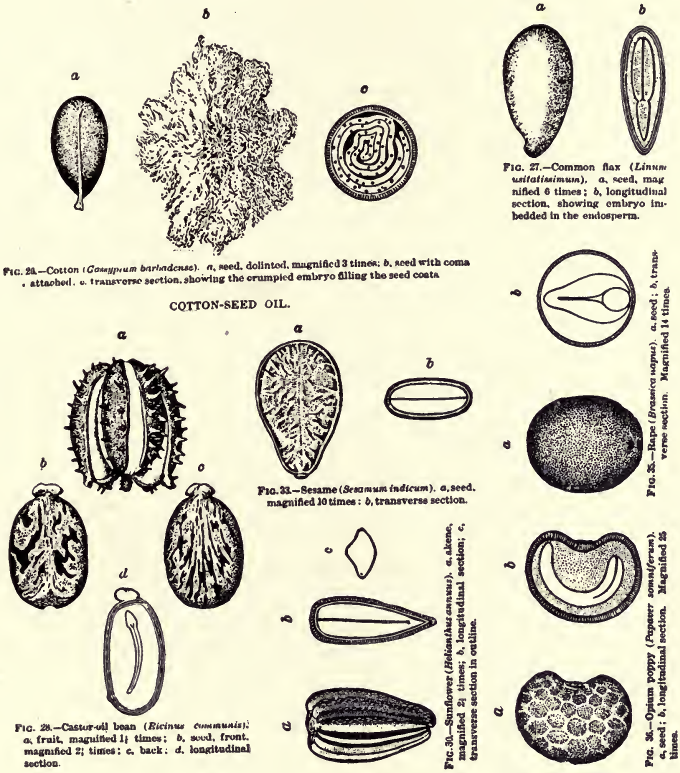

FIG. 27.—Common flax (*Linum usitatissimum*), *a*, seed, magnified 6 times; *b*, longitudinal section, showing embryo imbedded in the endosperm.

FIG. 29.—Cotton (*Gossypium barbadense*). *a*, seed, delinted, magnified 3 times; *b*, seed with coma attached; *c*, transverse section, showing the crumpled embryo filling the seed coats.

COTTON-SEED OIL.

FIG. 28.—Castor-oil bean (*Ricinus communis*). *a*, fruit, magnified 1½ times; *b*, seed, front, magnified 2½ times; *c*, back; *d*, longitudinal section.

FIG. 33.—Sesame (*Sesamum indicum*). *a*, seed, magnified 10 times; *b*, transverse section.

FIG. 30.—Sunflower (*Helianthus annuus*). *a*, akene, magnified 2½ times; *b*, longitudinal section; *c*, transverse section in outline.

FIG. 35.—Rape (*Brassica napus*). *a*, seed; *b*, transverse section. Magnified 14 times.

FIG. 36.—Opium poppy (*Papaver somniferum*). *a*, seed; *b*, longitudinal section. Magnified 25 times.

FIG. 34.—Oil-seeds. (Enlarged.)

are 76 in number, the principal ones being the castor (specific gravity, 0.964), olive, cottonseed (specific gravity, 0.9306, almost identical with linseed), resin, almond, beechnut, horse-chestnut, hazelnut, peanut, croton, sesame, colza, rape, mustard, with specific gravities ranging from 0.913 to 0.942. They mix thoroughly with each other and with the siccative oils, and the specific gravity of a pure linseed-oil can be easily counterfeited, even if its quality cannot be. Vegetable oils additional to the above, used medicinally and for soap, burning, and food, are 85 in number.

Vegetable oils, volatile and essential, number 134, or a total of 315 non-drying oils available for the purpose of adulteration. Add 80 animal and fish oils to the above, and it may be conjectured, the source from which a yearly supply from the whole world of 250,000,000 gallons of linseed-oil and other siccative oils can supply a demand for about 350,000,000 gallons of paints, varnishes, japans, and other uses, including the wastes of manufacture.

As before stated, if the flax is raised for the fibre, the seeds do not mature at the same time, hence they furnish a thin watery oil with a greater quantity of the albuminous substances, gum, sugar, and cellulose, called "mucosities," than the 54.44 per cent to 58.50 per cent found in ripe seed. Unripe or mildewed linseed is no more capable of furnishing a good oil than a green apple will make either good cider or good vinegar; an unripe grape, good wine; or grain or corn harvested in the milk will make good bread; and no amount of juggling in the subsequent manipulations of the paint manufacturer can replace the simple operations of nature, or ripen her unripe products or produce them from synthetical compounds.

The following is a comparison of the composition of a few of the principal oil-seeds:

SICCATIVE OILS.

Oil.	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.
Linseed	0.9352	77.40	11.10	11.50
Poppy-seed (black)	0.9270	76.57	11.41	12.02
" " (white)	0.9285	77.20	11.31	11.49
Hemp-seed	0.9307	76.00	11.30	12.70
Walnut	0.9288	76.65	11.46	11.89
		77.15	11.73	11.12

VEGETABLE NON-DRYING OILS.

Cottonseed	0.9306	76.40	11.53	12.27
Rape (winter)	0.9155	78.04	12.04	9.92
" (summer)	0.9165			
Earthnut or Peanut	0.918	75.73	11.57	12.70
Beechnut	0.923	76.65	11.47	11.89
Castor	0.9639	77.21	13.36	9.43

The grains yield oil similar in character to the other non-drying oils, viz.:

	Specific Gravity.	Carbon.	Hydrogen.	Oxygen.
Rye	......	76.71	11.79	11.50
Wheat	......	77.19	11.97	10.84
Barley and oats	......	77.50 to 75.67	11.96 to 11.43	12.78 to 10.69
Maize and lupine	......			
Peas and beans	......	77.40 to 76.00	11.30 to 11.15	12.70 to 11.50
Potatoes and rice	......			
Beets, etc	......			

The increase in oxygen in the grain oils is at the expense of the carbon.

MISCELLANEOUS NON-DRYING OILS AND SUBSTANCES.

Sperm-oil	0.945	78.90	10.97	10.13
Resin-oil	0.984 to 0.9910	79.27	10.15	10.58
Beef tallow	0.938	79.00	11.70	9.30
Beeswax	......	81.60	13.90	4.50
Spermaceti	......	81.60	12.80	5.60

The vegetable aromatic volatile oils from lemons, oranges, cloves, cinnamon, etc., are of the same chemical composition: Carbon, 88.25; hydrogen, 11.75. When they oxidize, it is at the expense of the carbon element. The diversities in their odor are due to a different arrangement of their atoms.

Poppy-seed furnishes a cold-pressed siccative oil of excellent quality. Being an imported article its price prevents its use except in the finer color paints. The exceptionally good results attendant on the use of French zinc oxide are principally due to the use of this oil. It dries slower than linseed-oil and faster than walnut-oil. It does not remain sticky so long as linseed-oil, not being so fatty, and takes up less oxygen. It is used for the finer classes of varnishes. It contains 20 per cent of non-drying and 80 per cent of drying oil. Linseed-oil clarified by sulphuric acid has generally taken the place of poppy-oil. Walnut-oil contains 30 per cent of non-drying and 70 per cent of drying oil. The cold-process oil is light colored with a pleasant smell and taste; after a short exposure to the sunlight it becomes as clear as water. The hot-process oil is characterized by a deep color and unpleasant odor; it has more mucilage in it, and does not dry as well as the cold pressed.

SPECIFIC GRAVITIES OF OILS AND FATS.

Poppy-seed oil	0.9245
Raw linseed cold-drawn oil	0.9299 to 0.932
Boiled linseed-oil	0.9400 " 0.942
Crude cottonseed-oil	0.9224
Refined yellow ditto	0.9230
Water-white ditto	0.9288
Menhaden-oil (dark)	0.9292
" " (light)	0.9325
Tanner's cod-oil	0.9205
Porgy-oil	0.9332
Resin, commercial yellow	1.0700
Resin-oil, first run	0.9835
" " third run	0.9887
" " other runs	0.9910 to 0.960
Crude Lima petroleum	0.839 = 7 pounds per gal.
Lard-oil	0.915
Whale- or train-oil	0.925
Sperm-oil	0.943
Porpoise-oil	0.937
Beef tallow	0.927
Mutton tallow	0.938

CHAPTER XXIII.

BOILING LINSEED-OIL.

J. Nelson Neil's Experiments.

THE study of the composition and properties of the siccative oils has been but little advanced since Mr. J. Nelson Neil was awarded the Isis Gold Medal of the Society of Arts in 1832 for a paper read before that society on "Oil Boiling and Varnish Making" (published in the Transactions of the Society, Vol. XLIX, Part II), which treats so exhaustively upon the modes of manipulation, recipes, and precautions to be used, that the paper is the foundation for all subsequent accounts and modes of manufacturing varnishes. The additions and modifications which have been worked out since that time have not materially altered the processes of Mr. Neil, either in the betterment of the quality of the varnish or the oil product, but relate more particularly to a shorter time and possibly less cost of manufacture than given by him, which comprised the application of direct fire to the kettles instead of the steam-jacket kettles and devices used by later experimenters and manufacturers.

The substances that act catalytically part with some of their oxygen in the oil, and become to a certain extent deoxidized, and again coming into contact with the air either mechanically blown through the combined mass of oil and driers, or by surface exposure in the settling-tank or barrel, recover their primal condition, and are ready to do the same work over again. It is the necessity for the reoxidation of the driers that causes the general adoption of the air agitation and steam processes now in general use for the boiling of oil and manufacture of varnishes, etc. These driers, without becoming materially altered, induce an alteration in the linseed-oil subjected to their operation. We may imagine this action as similar to that by which spongy platinum explodes a mixture of oxygen and hydrogen, or a platinum wire is kept red hot by the vapor of ether.

In properly prepared varnishes and paints from pure linseed-oil, the gain in weight after thoroughly dry is from 8 to 10 per cent of the vehicle, and it is heavier than water. Any paint that does not show a marked increase in weight in drying can be set down as one of the hundreds of bastard compounds that masquerade under the guise of paint, with more resin, fish-oil, and hydrocarbon substances in its vehicle than linseed or other siccative oils.

M. E. Chevreul's Experiments.

These experiments of Mr. Neil were followed by the experiments of Mr. M. E. Chevreul, who contributed a paper in 1856 to the *Annales de Chime*, corroborating Mr. Neil's deductions upon the drying of siccative oils, and by him clearly laid down, viz.:

First. That it is the absorption of oxygen by the siccative oils and the change of the oleic, margaric, and stearic acids of which they are composed, and the chemical combination with each other in the presence of oxygen into the linoleic and linolenic acids, that is the cause of their solidification, which term he thinks more clearly defines the action of the oil than drying, which in general may mean evaporation, which is a term adaptable to all liquid bodies, or rather indicates the removal of liquid from all bodies. This definition appears to be apropos to many of the latter-day cheap mixtures called paints; the difficulty experienced with some of which is not to have them dry in a reasonable time, but to have them keep liquid long enough to spread them at all.

Second. That the oxidation of the oil is a chemical process and naturally inherent in itself. The action of heat, as in boiling, hastens the drying or resinification of the oil by removing the water and mucosities. That all substances which can be used as driers must be such as are capable of parting with oxygen or dissolving in it; and being of themselves oxidizable in combination, they in that way increase its absorptive power. There is a class of driers (white copperas, for instance) which act catalytically, while mechanically suspended or in contact with the oil, and increase its oxygen absorptive power by their presence, but leave no increase of drying power when withdrawn.

Third. That manganese and litharge were the most powerful driers, and when used *in excess* and settled from the oil, they acted with greater power when used a *second time.*

Linseed-oil boiled 5 hours *without drier*, required 38 days to become thoroughly hard. When boiled the same period with new peroxide of manganese, it dried in 2 days. When boiled 6 hours with peroxide of manganese that had been used many times before, it required one-half day to dry firm and hard.

Fourth. That manganese driers for exposed paints appear to be less durable than red lead or litharge driers. They harden quicker and become more brittle, from the harder character of the soap they contain, which is further developed in hardness by the heat of the sun.

Fifth. The manganese-drier paints appear to peel more readily than red-lead driers, especially upon ironwork that has but few points or irregularities of the surface to which the paint can adhere. Hence such a paint for an iron surface must remain in a measure softer and more elastic, or else it will be thrown off or peel by the changes in temperature and the expansion and contraction of the metal.

Peroxide of manganese is electro-negative to iron and steel, and is noted for the freedom with which it imparts its oxygen to these metals. It is used in the manufacture of steel as a purge to burn out the impurities in it.

Analysis of Dioxide of Manganese or Pyrolusite (MnO).

Red oxide of manganese	84.05	to	87.00	per	cent.
Oxygen	14.58	“	11.45	“	“
Sesquioxide of iron	1.30	“	0.40	“	“
Alumina	0.30	“	0.00	“	“
Baryta	0.67	“	1.20	“	“
Calcium	traces	“	0.00	“	“
Silica	0.80	“	0.51	“	“
Water	5.80	“	1.92	“	“

Sixth. That linseed-oil heated until it lost one-sixth of its weight became thicker, unctuous, and viscid, and dried more readily, forming a tough, crude, turpentine-like mass, scarcely soluble in any other oil (printer's varnish). When linseed-oil is heated to 325° to 375° F. it will take fire and continue to burn without any further application of heat from without, until only tar or charcoal remains.

Nut- and poppy-seed oils also possess this feature, which is sometimes employed as a test of the purity of these oils. If these oils are adulterated to any great extent with fish, resin, or mineral oils, they will not continue to burn after ignition without a further addition of heat.

Prof. Chevreul's experiments to show the effects of atmospheric gases on the drying of linseed-oil were as follows:

Four panels of wood were painted on one side with white lead and on the other side with zinc oxide, the vehicle being raw linseed-oil.

No. 1 was placed in a closed glass vessel exposed to carbonic-acid gas.
No. 2 was placed in a similar vessel exposed to confined air.
No. 3 “ “ “ “ “ “ “ free air.
No. 4 “ “ “ “ “ “ “ oxygen gas.

The results were as follows:

	After 24 Hours.	After 72 Hours.
No. 1. Carbonic-acid gas.	The white lead nearly set.	Set but without adhesion to the wood.
	The zinc oxide still fresh.	Absolutely fresh.
No. 2. Limited air.	The white lead nearly dry.	Perfectly dry.
	The zinc oxide set but not dry.	“ “
No. 3. Free air.	The white lead nearly dry.	“ “
	The zinc oxide set but not dry.	“ “
No. 4. Oxygen gas.	Both perfectly dry.	“ “

Professor Vincent's Experiments.

Prof. Chas. W. Vincent's experiments in 1859 were upon the line of boiling oil without the presence of driers, and that a high temperature was not necessary. The temperature used by Mr. Vincent was that due to steam at 40 pounds per square inch, 267° F., used in a steam-jacketed kettle in connection with mechanical agitation by revolving blades and a current of compressed air moderately heated by the act of compression. This process is that in general use at present in the manufacture of linoleum, and it is believed that the Germans practised this method many years preceding 1859. Professor Vincent's conclusions, drawn from experiment, were that air blown through the mass of heated oil *is not* as important a part of the process as many have assigned to it, and in reality effects nothing toward making the oil a drying one. He boiled linseed-oil with air alone, *but without driers*, for three days consecutively, keeping up a high temperature the whole time, and the resultant boiled oil required precisely the same time to dry as the raw oil from which it was prepared. The body, however, had become so much increased that its consistency was more that of a varnish than an oil. In the oil subjected to the heat alone for the same time, without any air, except such as came to it in contact with its surface in the kettle, there was no such increase in its consistency as in the former case; the oil simply became more greasy, had less difficulty in penetrating the capillary tubes of paper, plaster, etc., than it previously had, and had decidedly *less* drying power. The oil that had been boiled with the air-blast was less greasy and had a greater consistency. Briefly, the surface exposure to the air and the heat secured a sufficient amount of body. The driers produced any required shade of color in the oil and reduced the time of drying from 3 and 4 days, for the raw oil, to 6 hours in the summer and 8 hours in the winter for the boiled. Boiled oil that is subject to long voyages at sea is apt to become fatty and not free working. This is due to the agitation it gets from the motion of the ship while it is under the increase of temperature due to the hold or cargo space in the ship, being, in fact, a long-continued low-temperature and agitation process of boiling. The manufacturer guards against this result by adding to boiled oil for shipment by sea, about one-fourth its volume of raw oil, the oil becoming brighter in consequence of the addition. Professor Vincent's steam-kettle process of boiling gives an oil of a lighter shade than the direct fire or high-temperature process. In both processes, acrylic acid ($C_3H_4O_2$), a monobasic acid, is produced by the oxidation of acrolein. Acrylic or acroleic acid when purified, is a colorless liquid of a slightly empyreumatic odor, lighter than water and mixable with it in all proportions.

Acrolein (C_3H_4O) is the acid principle produced by the destructive distillation of fatty bodies, resulting from the decomposition of glycerine ($C_3H_8O_3$). Acrolein is a colorless, limpid, strongly refracting liquid, lighter than water, boils at 126° F.; vapor density, 1.897. Its vapor is so intensely irritating that a few drops diffused in a room are sufficient to render the atmosphere unsupportable. It burns with a clear bright flame, and dissolves in 40 parts of water and readily in ether. The solutions at first are neutral, but gradually oxidize and turn acid in contact with the air. Under water it changes into a resinous substance (disacryl-resin) and the water becomes charged with acrylic, formic, and acetic acids. The vapor of acrolein passed through a red-hot tube is decomposed with the formation of water and charcoal. Its vapor is highly corrosive to iron bodies.

Acrolein is developed by the decomposition of the mucosities in the raw linseed-oil under the influence of the boiling heat, and indicates the slower decomposition of these substances in a raw-oil vehicle for a paint. The slower process of solidification of the raw oil enclosing them, as it were, in a film of the vehicle, to develop later by decomposition into a destructive agent of the paint. The pigments in the paint may delay this decomposing action for a time, but cannot wholly prevent it, and in many cases hasten it. The removal or destructive change of these mucosities is absolutely necessary in baking japans, varnishes, japan driers, and linoleum; and if found detrimental there, it must necessarily follow that they are equally so in a paint oil. The decomposing point in a pure linseed-oil made from thoroughly ripe linseed is nearly 100° F. higher than in an oil made from green or damaged linseed.

Professor Sacc's Experiments.

Professor Sacc's experiments in brief were, 2500 grains of oil boiled for 10 minutes only, with 30 grains each of litharge and red lead, and weighed after 24 hours' exposure to the atmosphere, the oil had lost only 60 grains. This sample increased 20 per cent in weight after complete resinification. A second sample boiled until there was a loss of 5 per cent in weight of the oil, the product assumed a molasses consistency, and did not resinify after 15 days' exposure to the atmosphere. A third sample boiled to a loss of 12 per cent became a caoutchouc-like mass that the atmosphere had no effect upon whatever. It was insoluble in alcohol, ether, chloroform, and bisulphide of carbon; boiling naphtha only dissolved traces of it. The only action which dilute acids had upon it was to extract a small quantity of the oxide of lead due to the driers. Hydrochloric acid dissolved it slowly, while concentrated sulphuric and nitric acid dissolved it rapidly, as they do all vegetable and animal oils and tissues. This substance was in fact identical with the product obtained by the modern process of boiling oil for the manufacture of linoleum.

Linseed-oil submitted to a dry distillation (without boiling) gave off a white vapor (acrolic) from which was condensed a colorless oil (acrolic acid), having the odor of fresh bread, then expanded and yielded a distillate, a brown empyreumatic product; finally, a mass resembling jelly and caoutchouc remained.

The Sulphuric-acid Process.

This process of boiling oil has been adopted by a number of manufacturers. It furnishes an oil of light color which dries well and rapidly, mixes with all pigments without leading to any discoloration. Whites retain their purity of tone unchanged, but with all these points in its favor, the process cannot be recommended for the preparation of a vehicle to be used for a ferric protective coating. Briefly, the oil is first treated with a dilute sulphuric-acid bath (containing about 30 per cent of sulphuric acid) which is agitated with the oil by the air-blast to *dehydrate it,* but is said to be not strong enough to carbonize it. After standing to allow the oil and acid to separate, the oil is run off into the usual steam-jacketed kettle heated to about 267° F., air is blown through the mass, while a solution of manganese linoleate in some hydrocarbon spirit (probably benzine) is added gradually during the process of heating and blowing. Cautionary care is required *not to add too much* of this material. It is the writer's opinion that this caution should extend to the point of not adding any manganese asociated with any hydrocarbon vehicle to the oil, and that prohibition should extend to the use of any sulphuric, nitric, or other caustic acid of any strength to the oil in its preliminary stage. It is almost impossible to clear an oil of either high or low specific gravity, of any acid of whatever strength of solution to which it may be exposed. More or less of the clarifying acid will be held in the oil either free or in combination with the water in the oil, that even a long washing with water, aided by an air-blast agitation, *will not remove.* Kerosene, naphtha, gasolene, etc., are purified by treating with sulphuric acid and then thoroughly washed with water and a long agitation by the air-blast, and are then often found to contain acid enough to perforate the tin cases in which they are shipped. The slight improvement in the color of the boiled oil by this process is a very poor recommendation for its use. The same results are obtainable by the ordinary steam-kettle process, using well-known mineral substances; for instance, the zinc and manganese salts will remove or throw down the mucosities, clear the oil to any desired shade, and cause it to dry promptly, while the water in the oil will be evaporated, naturally by the heat, and the dangers of the sulphur element avoided.

Thorp's Experiments with Driers.

The action of various mineral and metallic driers upon linseed-oil in the process of boiling to determine their effect on the color of the oil and the time of drying were made by Mr. Frank H. Thorp, S.B.*

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* *Journal of Chemical Industry,* Volume IX, p. 628, 1890. Reprinted in the *Scientific American Supplement,* No. 757, Volume XXX, June 5, 1890.

The oil experimented upon was in every case from the same barrel, and was a very light-colored, cold-pressed, Calcutta raw linseed-oil, *specific gravity*, 0.93. The weight of oil under test was in each case the same, 50 c.c. weighing 45.7 grms. The several samples were treated in glass beakers arranged in a sand-bath under temperatures from 200° to 300° F. In general, the temperatures from 230° to 275° F. gave the best results. The time of actual boiling was from 1½ to 2½ hours, and the percentages of driers varied from less than 1 per cent to 2 per cent by weight of the oil treated. Litharge furnished an almost colorless oil of firm film, drying in from 6 to 10 hours. Lead carbonate, lead acetate, and lead borate, each furnished slightly colored oils with good films, drying in the order named, in 10, 12, and 20 hours. Red lead, lead chloride, and lead tartrate furnished dark-colored oils of good films, drying in from 20 to 24 hours. Red lead and litharge, 2 per cent of each, also the other lead salts mentioned, with larger percentages than two of each, gave dark-colored oils, all with firm films, drying in about 24 hours.

Of the lead driers, litharge gave the best results both in color, film, and drying qualities. Care was necessary in the use of this drier, to not overheat the oil, thus deepening its color. The zinc salts, the acetate, borate, citrate, oxide, and sulphate, furnished nearly colorless or slightly colored oils with fairly good films, but their time of drying was from 36 to 46 hours. Larger amounts of these driers than 2 per cent shortened the time of drying, darkened the color of the oils, and they did not clarify satisfactorily.

The acetate and borate are the best of the zinc-salt driers, but none of them act catalytically upon the oil as the lead and manganese driers do, but act mechanically or only while present (like white copperas), to throw down some of the mucosities, but do not cast them all out, or set up the combination changes necessary to form the linoleic compounds required in a good drying oil. The manganese salts, viz.: the acetate, borate, sulphate, oxalate, and tartrate, all gave colorless oils, drying with good firm films in from 20 to 36 and 40 hours. The citrate and formate gave slightly darker-colored oils, drying in about 24 hours with good firm films. The manganese borate with quantities varying from 1 to 3 per cent of the oil and with temperatures of 220° to 230° F., gave the best colored and drying oils obtained in the whole line of experiments. The other manganese salts with larger than 1 per cent of driers with temperatures from 250° to 300° F., gave colored oils of unsatisfactory drying power, some of the samples being tarred. No definite conclusion can be drawn from Mr. Thorp's experiments as to the relation between the quantity of driers dissolved in the oil, and the time of drying of the oil. The action of the several classes of driers, as well as the various members of them, was erratic and the drying result appeared to be governed quite as much by the temperature of the bath, time of boiling, and agitation of the oil during boiling, as by the chemical employed. One per cent by weight of litharge and the lead driers, and two-tenths of 1 per cent of the manganese salts, were all that were required to give good bright-colored oils of good drying qualities with firm films, and not all of these amounts of driers were taken up by the oil, but some were recovered in the residuum.

The sulphate of zinc boiled with linseed-oil simply removes the vegetable and mucilaginous substances that impair its drying power; it does not impart any catalytic power to the oil to draw oxygen from the air.

Peroxide of manganese, umber, red lead, and litharge, all dissolve in the oil and impart oxygen to it, and act catalytically to take up more oxygen from the air to renew what they have lost, and in so doing further oxidize the oil.

Thorne and Brin's Oxygen Process.

In this process for oxidizing oil, pure, or nearly pure, oxygen gas in a finely divided stream is poured through the oil at natural temperatures, or moderately heated, if desired. The process occupies from 2 to 7 hours, but a small quantity of the usual driers shortens the time of oxidation. The color and drying qualities of the oil oxidized by this process are excellent. The consumption of oxygen gas varies from 2000 to 4000 cubic feet per ton (250 gallons) of oil, according to the degree of oxidation required.

The principal difficulty in this process is in generating the supply of oxygen gas, which requires a more complicated plant, chain of operations, and intelligence on the part of the workmen than that connected with the quicker processes of the bung-hole boil, where a bung-starter, a scoop, and a dish of metallic salts are all that are necessary for a manufacturing outfit.

In the manufacture of corticine (resembling linoleum) the oil is oxidized at a high heat, 350° to 500° F., until it begins to thicken and get ropy. The result is not only a loss by evaporization, but the oil acquires a peculiar sickish smell that no subsequent treatment or step in the manufacture is able to remove.

The present-day process of boiling oil upon a large scale as practised by most of the crushers of linseed is to dissolve 4 pounds of lead oxide or litharge, or both, in 5 gallons of well-aged and settled linseed-oil at a temperature of about 250° F. for a short time or until all of the oxides are absorbed.

This mixture if allowed to cool will harden into a firm cake of gum (linolate of lead). This product while still hot is mixed with 40 to 50 gallons of linseed-oil heated to the same degree to coagulate the albumin, and the mixture allowed to settle. Five hundred or more gallons of this mixture are made up, and while hot are mixed with a large tank (5000 gallons or so) of raw linseed-oil also heated to about 200° and thoroughly stirred together. This is *commercial boiled oil,* which varies in character according to the quality of the linseed-oil used in any stage of the process, also in the proportion of the oxide oil to that in the large tank, 4, 6, 8, or 10 to 1, etc. Lead oxide and a small quantity of manganese oxide make a better drying oil than the red lead alone.

Varnish-makers make this liquid drier for use by local painters, who remove 4 or 5 gallons of raw oil from the barrel and replace them with the same quantity of the liquid drier, and then roll the barrel around or stir up the mixture with a paddle-stick for their "bung-hole" boiled oil.

Some large users of paint oil think that this make of "bung-hole" boiled oil is as good as that supplied by the large manufacturers; but this is doubtful, as all of the albuminous substances in the bung-hole oil are retained unchanged, and they are subject to a future decomposition that the 200° of heat in the cooking of the large tank of oil coagulates, and they settle out on standing.

Lead- and manganese-oxide driers made from resin, or resin-oil, are marketed on a large scale at 18 to 20 cents per gallon, while a properly made linseed-oil drier cannot be furnished for less than 3 to 4 times that price.

Double-boiled oil means that a *double dose* of drier and resin-oil has been put through the bung-hole process. The more drier the poorer will be the oil product.

No two manufacturers of boiled oil furnish an oil of the same character or quality, owing to their different manner of cooking it and the amount and kind of drier used, etc. The name "boiled oil" represents about as uncertain a product as a mixed paint, and is simply a trade-name for an extremely varied composition.

The reputation of the dealer or manufacturer is the best guide. Adulterations by the use of resin-oils are to be especially looked for in all commercial grades of boiled oil.

Boiled oil is a misnomer. Linseed-oil never boils; if it did it would decompose into a permanent gas. The degree of heat applied in the process of so-called boiling by careful manufacturers is only that necessary to evaporate some of the water natural to the oil. This degree and amount of heat also coagulates the mucilage and albuminous substances, so that they are released from the acid oils, and, by their greater weight, are deposited as soon as the oil comes to a state of rest after the heating process. In oil from ripe linseed, if given time to age after crushing, the mucosities and some of the water in its composition (about 5 per cent), that is loosely held in combination, will settle and can be filtered out or drawn off, leaving the oil bright and clear, and with a minimum amount of water to be evaporated in the process of drying as a raw oil. Storage in tanks for 3 or more months still further improves the oil, especially if the tankage is kept at a moderately warm temperature. This fact is taken cognizance of by the varnish manufacturers, who require the best quality of linseed-oil for their products, and from the better prices they receive for their wares, can secure the best qualities of oil in the market at a price that the manufacturers of cheap paints cannot compete with. Storage of three or more millions of gallons is carried by some of the best varnish and linseed-oil trade dealers. The natural result of such selection and storage is, that the oil is well aged, clear, and bright, and can be depended upon as a vehicle, unless afterward adulterated or abused in its application.

As stated before, all driers are injurious to linseed-oil, and the marked inferiority of trade boiled oil to raw linseed-oil is due to the driers used, whether liquid or solid, and not wholly to the removal of the water and mucosities in the boiling process. The salts and oxides of metals that constitute the solid class of driers, that enable the oil to dry promptly, are generally added in great excess of the amount actually necessary for aiding the natural tendency of the oil to dry. That portion of the driers in excess remains in the dried coating, and acts as a carrier of oxygen, to attack the pigment; and the subsequent failure of the coating is assured.

CHAPTER XXIV.

DRYING OF LINSEED-OIL.

MULDER's experiments in the drying of siccative oils determined that there were two periods in the drying of a paint, oil, or varnish coating. The first period occurs in the early months, and is wholly due to the changes in the drying elements of the oil, and while these changes are in progress, the covering is always dry to the touch and remains elastic. This period is of longer duration if the coating is not exposed to the direct rays of the sun. During the period, 100 parts of the oil at ordinary temperatures increase in weight to 111 or 112 parts, but when warmed to 170° F. it loses 4 to 5 parts. In the direct sunlight for all the period of drying, the oil *gains* about 7 parts.

During the second period the oil becomes hard and firm as a resinous coating, the change being in the non-drying elements of the oil. The increase in weight of the oil is not so great, because the breaking-up of the glycerine element has taken place in the first period. These total changes amount to about a quart of oil in 1000 square feet of painted surface.

The influence of heat in drying a paint or varnish is apparent when it is considered that in the ordinary drying of either to a firm, hard coating, 21 per cent of oxygen has been absorbed from the atmosphere or driers, yet a further exposure to the heat of the sun until the coating becomes hard and resinous ensures a loss of 3 to 5 per cent of this amount. It is to be recommended that this drying and loss be had while the coatings are still elastic, because this loss in substance (due to the changes in the non-drying oil) takes place while the vehicle is soft and elastic enough to adjust itself to the loss in volume.

Oil or varnish dried in the direct hot rays of the sun are not as durable as when dried in the shade, the effect of the sun being to evaporate the volatile elements of the glycerine ethers instead of absorbing them into the non-drying or fatty acids of the oil. A frost on a drying oil or paint is fatal to its integrity; the coating will peel in strips and cannot be restored; but paint dried in clear cold weather (not frosty weather, that leaves a sweat in and on the coating, as the temperature rises) lasts longer than a sun-dried coating.

It is probable that the cold-dried coating lasts longer for the reason that its change into the hard-soap compound has been delayed, and being more elastic than the sun-dried, the bond between the pigment, oil, and surface covered is more effectually made. Hence some lead in the from of a drier is, therefore, an advantage in an oil compound or paint, if the pigment does not contain it. The manganese driers are especially unreliable if applied in cold or unfavorable weather.

The percentage gain in weight of a cold-drawn raw linseed-oil, exposed for drying under different conditions, was as follows:

Days Exposed.	In Darkness.	Under Unclouded Glass.	Under Blue Glass.	Under Yellow Glass.	Under Red Glass.	Under Green Glass.
10	.000	0.126	0.089	0.012	0.009	0.005
20	.001	0.236	0.245	0.041	0.027	0.023
40	.003	0.258	0.376	0.181	0.082	0.139
60	.007	0.298	0.388	0.319	0.178	0.269
90	.013	0.272	0.357	0.417	0.338	0.401
120	.018	0.273	0.360	0.442	0.376	0.438
150	.035	0.300	0.399	0.474	0.441	0.485

After 150 days the gain in weight was the greatest in the following order: green, yellow, red, blue, and uncolored. The application of a dry heat at temperatures of 150° to 170° F. dries a raw oil from 30 to 50 times faster than an open-air exposure under the general conditions of summer weather. Light, heat, and air are all necessary elements to properly dry an oil-paint or varnish coating of any quality. The slow-drying oils gain more weight than the quick-drying.

Raw linseed-oil has a specific gravity of 0.9299 to 0.931, and the same oil boiled, that of 9.411. One hundred parts of drying and non-drying elements in the raw oil in the process of kettle-boiling lose 8 parts of glyceride ether and one part of the carbon and hydrogen from the non-drying oil or fatty acids. This is equal to 9 parts in all, leaving 90 parts that absorb 21 parts of oxygen from the atmosphere when the oil is fully dried, the 100 parts of the raw oil becoming 111 when dry.

The presence of the glycerine ether and the changes it effects between the oleic, stearic, margaric, palmitic, and other acids forming the non-drying oil and the drying elements to form the linoleic compound, appears to be necessary, as Mulder indicates, who added oxide of lead to the oil that formed with the glycerine a hard-lead soap. The drying-oil acids were then washed away by ether, the ether was drawn off, and the strictly siccative part of the oil set free. When this oil was spread and exposed for drying, it gained in weight 8 per cent in 3 days, 14 per cent in 7 days, 17½ per cent in 30 days, but did not become fully dry in many months.

A putty made from thick glycerine and dry white lead or litharge, or both, will harden in from 15 to 45 minutes.

The conclusions of Mulder and many other experimenters in this line, as well as those of practical painters, are: That any metallic salt used as a free or bung-hole drier, or as a heat-combined drier, that is so energetic in action as to *destroy* the glyceride element instead of *aiding it* to effect its change into a drying oil, is an injury. The oil can be made to dry by evaporation by adding volatile driers, but it does not form a firm reliable coating, like that produced by a natural resinification.

The London *Journal* notes that Lippert, experimenting with oils and varnishes in order to observe the effect of the absorption of oxygen during the process of drying, finds that for boiled linseed-oil the less drier used the better, whether the drier be a manganese resinate or lead oxide. After its application upon a surface, a coating of this kind increases in weight while drying. The higher the proportion of drier, the sooner is the maximum of absorption reached, and the sooner, also, the coating begins to lose weight again. Conversely, the smaller the proportion of the drier, the larger is the total weight of oxygen taken up. After 4 weeks, the varnish containing 2 per cent of manganese had commenced to soften again, and stuck to the palm of the hand. The preparation containing only 0.15 per cent of manganese was distinctly the best. With litharge, also, the larger the proportion of drier the sooner the varnish attained its maximum weight, and the less total oxygen was absorbed. All the films were equally hard to the touch when they had reached their maximum weight; but after 4 weeks they softened again—this being more especially noticeable with the specimens containing much of the drier. Additions of litharge above 2½ per cent made no appreciable difference in the absorbing power; while for practical work the proportion of the lead ought evidently to be kept lower than that permissible with the manganese salts (see Thorp's Experiments, Boiling Oil, Chapter XXIII.). The reason why such coatings soften again after becoming dry is not yet known. It may be found to depend on the presence of an excess of drier, or of an unsuitable one. It does not prove adulteration with rosin or rosin oil. It may be due to oxidation of lead linoleate into a liquid turpentine-like body by prolonged exposure to the air. Science indicates no better way of testing a drying varnish than by the finger.

Prof. Max Pettenkofer removed the non-drying acids from freshly dried linseed-oil skins by ether, leaving an elastic caoutchouc-like substance, which by degrees hardened and became brittle. On further exposure to the air it separated easily into thin flakes; in fact, it hardened and cracked like the fossil resins or the coniferæ crude gums.

These deductions from a long chain of closely and carefully conducted experiments, not only in the laboratory, but in the application of oil, paint, and varnish coatings, with all classes of pigments, spread over ferric, wood, and mineral surfaces, appear to be ignored in many, if not in most, of the present-day compositions of paints and oils.

The larger amount of mucilage in all unripe or damaged linseed and other vegetable oils, when freshly made, or that have been extracted by the bisulphide of carbon, the hot or steamed seed processes, deteriorates the quality of the oil, and such oil even if it is to be kettle-boiled, is benefited by long standing to allow some of the "mucosities" or "drops" to settle. The amount of these preliminary "foots" is from one to one and one-tenth part in one hundred parts of oil. The greener or poorer the class of seeds from which the oil is made the greater will be the amount of "foots."

CHAPTER XXV.

LINSEED-OIL TESTS FOR ADULTERATIONS.

There are many methods of testing the purity of linseed-oil. The specific gravity test is of small moment, even if not altogether unreliable, as the commercial adulterant oils (over one hundred in number) vary in specific gravity only seven-hundredths of a degree Baumé, and no reliable chemical test has been found that is practical for the ordinary analyst.

One difficulty lies in procuring a chemically pure oil to make the comparison with the reactions caused by sulphuric and nitric acids, and caustic-soda treatment for the color changes in the sample tested. The linseed for such an oil must be picked over with the greatest care, selected from fully ripe and full-weight seeds, and pressed in seed bags that have never been used before.

The result of an application to a large number of the most responsible oil-seed-pressing firms, was that not one could furnish a sample with less than 5 per cent of other seed-oil in it, and most of the best commercial brands contained over 12 per cent.

Approximation chemical tests are numerous, but in all cases a sample of known quality of linseed-oil should be used for comparison, even if it is not a chemically pure oil. Abbe's and other refractometers are used to test the purity of linseed-oil, but their use is too complicated for any one but an experienced chemist.

All the fatty oils change color when brought into contact with strong sulphuric acid. If a drop be added to 8 or 10 drops of an oil placed on a glass plate resting on white paper, the following colors are immediately produced. Olive-oil turns a deep yellow, gradually becoming green. Sesame-oil, a bright red. Colza-oil, a greenish-blue aureola. Poppy-seed oil, a pale yellow with a dingy gray look. Hempseed-oil, a distinct emerald green. Linseed-oil turns brown-red, changing to a black brown.

Prof. F. C. Calvert's chemical method of testing oils by acids, for the color changes, is given in full in Watts's Dict. of Chem., Vol. IV, p. 183.

Mineral oil or petroleum in any form cannot be added to linseed-oil to exceed 5 per cent without affecting its drying; and 10 per cent prevents its drying other than as a thin skin impervious to the air, and the oil remaining green beneath is liable to blister or peel on exposure to sunlight. It does not bond to the pigment or surface coated.

If a tin plate coated with a mixture of a vegetable and a mineral oil be viewed at different angles in strong sunlight, the mineral oil can be detected by the iridescent or metallic play of color, which petroleum imparts to all vegetable oils. So characteristic is this, that a little experience will enable a painter to readily detect mineral oil when present even in a small quantity. This feature is in some degree disguised or palliated by treating the mineral mixed oil with caustic lime, chalk, etc., and adding an excess of strong free driers, which may suppress the iridescent hues; but if the sample is ignited, the marked pungent odor of burning petroleum vapor is readily recognized.

Cottonseed-oil, a semi-siccative oil, was formerly mixed in large quantities with linseed-oil. Its specific gravity, color, taste, and odor are almost identical with linseed-oil. It requires a large amount of driers either compounded with it by heat or as free driers to enable it to dry. Its tendency at the best is to harden and crack the overlying coatings; also to crack in cold weather, from its non-elastic condition due to the driers used. Crude cottonseed-oil treated with strong ammonia mixed with 3 parts of water, gives an opaque brown color. Refined cottonseed-oil, similarly treated, gives a brownish or dull opaque yellow. Pure linseed-oil similarly treated for comparison, gives a bright, but semi-transparent yellow. Mixtures of both oils give an intermediatory color, that a little experience will enable a painter to determine approximately the amount of the mixture.

A quick test by cold is to place a sample of the cottonseed-oil, mixture on a piece of glass alongside of a known sample of linseed-oil, and place the glass in a refrigerator or on a piece of ice. In a short time the impure sample will become discernibly thicker than the linseed-oil.

Crude cottonseed-oil produces a brown deposit on a piece of bright copper foil (to be had from all dealers in chemicals) if left in contact with it in a warm place for 3 or 4 days. The price of cottonseed-oil of late years has become so nearly that of linseed-oil that its use to adulterate the latter has sensibly diminished. There is, however, a combination of the damaged seed oils from both crops, for which there is always a demand to furnish a mogrel linseed-oil at a cut-rate price.

Resin oils are freely used to adulterate linseed-oil, even by firms whose business reputations should warrant more honest wares. Resin mixes readily with linseed-oil, and whether its grade be light or heavy, it cannot be detected by its specific gravity. For a quick test of its presence, shake up a spoonful of the sample with 5 times the quantity of strong alcohol; pour off the alcohol and add to it a clear solution of sugar of lead; a cloudy precipitate shows the presence of resin.

Resin-oil can also be detected by the remarkably nauseous aftertaste produced by it when touched by the tongue. The odor of the oil is not recognizable in the sample unless ignited, when it becomes decidedly different in odor from ignited linseed-oil. If the cork of the sample bottle squeaks when it is twisted around in the neck of the bottle, no further test is necessary to denote its presence.

Linseed-oil adulterated with resin-oil of any grade is readily detected by passing a current of chlorine gas through the sample oil, which is rapidly blackened if any appreciable amount of resin is present.

Resin-oil is especially to be looked for in boiled oil. It never hardens completely, and makes the coating "tacky." If any considerable amount of resin is present in a linseed-oil that has received an excess of driers to harden the coating, the coating will be brittle and crumble easily on a short exposure to the atmosphere, particularly in summer weather, or by exposure to heat.

Menhaden and porgy fish-oils are used freely to adulterate linseed-oil, especially in many of the mixed paints and pastes. The price of these oils is only about one-half that of a poor linseed-oil. Fish-oil in the twentieth century, used as an adulterant of linseed-oil, comprises almost anything from a whale to a mossbunker, with the oil from dead animals frequently added to help out the abomination. The fish-oils dry slowly, but surely, if fortified by strong, free driers. Fish-oils used for a tin-roofing paint will stick longer than a linseed-oil paint, as they do not dry so hard. They are more affected by cold than linseed-oil, and whatever paint coating is spread over one with a fish-oil vehicle will probably peel in a short time.

Crude menhaden-oil when cold has but little odor, and in color closely resembles linseed-oil. By strongly heating a sample the fishy odor is developed. Skilfully mixed, the odor is hard to detect, even when moderately heated.

Place a sample of a known quality of linseed-oil and one of the oils to be tested, in separate test-tubes, cork, and then heat together in a hot water-bath; if the suspected oil gives off an odor of acrolein (oxidized glyceride) similar to that of the smoldering wick of a tallow candle, fish-oil of some grade and amount is present.

One of the most reliable tests of the purity of linseed-oil, and one that does not have to be *felt for* as in the preceding tests, and is equally available, is, viz.: Add to 100 parts of the oil by weight, one-half of one per cent by weight each, of litharge and red lead well stirred together. Heat in any convenient vessel, and in any manner, until an immersed thermometer reaches 480° to 500° F. A feather from a feather duster or chicken's wing will answer instead of a thermometer. If the feather when dipped in the hot oil curls up with a crackling sound, it indicates an approximate temperature. A small current of air from a bellows or other source should be blown through the oil as it is being gradually heated. A small glass tube and a piece of druggist's rubber tubing are readily available for this part of the apparatus. Small samples are taken out from time to time and cooked on an iron plate. As soon as the samples appear stringy when cold, allow the oil to cool, stirring it constantly during the cooling. If the oil is solid and firm when cold the sample is of good quality. A poor oil will be sticky and more or less fluid, and of bad odor.

Animal oils can be detected by their odor when the sample is heated, also by the addition of nitric or sulphuric acid, either of which gives an intense-red color to fish-oils. The adulteration of mineral oils is readily discovered by the process of saponification, when these substances rise to the surface. The saponification number, or the number of milligrams of K.HO required to saponify linseed-oil, is 190.2 to 192.7. This number for many adulterated oils is as low as 180. The iodine number of linseed-oil is 158.7 to 159.78; that of fatty acids, 159.85.

It is frequently necessary to clarify linseed-oil. The following are a few of the methods:

Heat the oil slowly up to 300° C. (570° F.) either by itself or with the addition of from 1 to 5 parts of either caustic lime, carbonate of lime, calcined magnesia, or carbonate of magnesia, and keep the oil at the above temperature for 2 hours, and then allow it to cool uncovered and undisturbed. Transfer it to a settling-tank to deposit and clarify. When clear transfer it to another vessel. Clarified oil should not be kept in contact with the deposit or "drops."

Mulder recommends the clearing of turbid linseed-oil by washing it with its own volume of warm water containing some common salt.

Sulphuric acid is used for clarifying linseed-oil, particularly adulterations of it. Its action is to carbonize the fibrine elements of the fish-oils and the mucilaginous substances in the vegetable oils, and to deposit them in the so-called "foots" or "drops." Its action is injurious to linseed-oil in general, for it removes by carbonization a part of the fatty acids, or non-drying elements, *and all* of the glyceride ethers, the latter being essential to the changes necessary to form a firm, hard coat from the oil when dry. Acid-treated oils are liable to dry on the exterior only, and never become hard or firm. Acid-treated oils require long, careful, and *repeated* washings with warm water in the form of an air-blown spray through the body of the oil in a deep tank to eliminate the acid, which is seldom thoroughly done. The acid, besides delaying the drying, will attack the metallic-base pigments afterward associated with it in the paint.

Graphite and carbon pigments are less affected by sulphuric acid in the oil than any other class of pigments.

Graphite paint-skins detached from the metallic plates on which they had been spread and dried, when immersed in 5 per cent solutions of sulphuric acid, lost in weight from 1.5 to 1.7 per cent, but were not affected in lustre, strength, or elasticity.

This result indicates their superior qualities for heavy coatings for roofing paint, and in other locations where any sulphur element can reach them, whether from the vehicle or the atmosphere.

The results of Mulder's experiments with sulphuric-acid-treated oils to ascertain their qualities were that they did not begin to dry materially under 8 days. At the end of 3 months the samples had gained 15 per cent in weight, but lost 3 per cent of this when heated to 150° F. for a short time. Also a strong heat from the sun for a number of summer days produced the same effect.

Pure linseed-oil, not treated, gained 10 per cent in the same period and lost 2.5 to 3 per cent on heating it. The acid did not affect the *drying* elements in the oil, only the *non-drying* ones, as noted before.

The colors of the acid-treated oils were not materially affected by the process; generally, they were brighter for the treatment.

Sulphuric-acid-treated oils being naturally of a fatty or non-drying character, if ground in a hot mill will develop this feature more fully.

Sulphuric acid in the oil or pigment appears to take kindly to wooden surfaces as a priming coat; at least the disintegrating effect of the acid is not so marked as upon metal. All sulphuric-acid-treated oils have a tendency to increase the galvanic action in all paints made from them, that are spread on wooden surfaces. When used on metallic bodies electrolysis is increased.

The following table * gives the weight in grains of sulphur in a gallon, of a number of the oils when burned by means of a wick floating in the oil, and condensing in a sulphur apparatus the vapors of combustion, the same way as sulphur is determined in coal-gas:

Name of Oil.	Grains of Sulphur Per Gallon.
Linseed-oil (La Plata)	trace.
Cottonseed-oil	trace.
Olive-oil	none.
Groundnut-oil	none.
Sperm-oil, ordinary	2.3
“ “ bottle-nose	3.1
Cocoanut-oil	3.7
Neatsfoot-oil	4.7
Cod-oil	5.8
Rape-oil (Jamba)	11.3
“ “ pure brown	14.2
“ “ ordinary brown	17.4
“ “ brown, refined with sulphuric acid	16.8
“ “ “ “ “ fullers' earth	10.0
“ “ “ (Ravision's)	19.1
Russian mineral oil, crude, 0.908	20.5
“ “ “ burning	10.3
American mineral oil, water-white	8.1
“ “ “ burning	16.3
“ “ “ safety	14.0
Scotch mineral oil, used for making gas	49.8

Water in Linseed-oil.

Pure raw linseed-oil contains over 5 per cent of combined water, and the commercial or poorer grades of the oil frequently contain 10 per cent. Twenty per cent of water can be stirred into linseed-oil by a painter's paddle, and over 10 per cent more, if the mixture is run through a mixing-mill, either with or without a pigment.

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* *Chemical News*, also *Scientific American Supplement*, July 20, 1895. Experiments by **Wm.** Fox and D. G. Riddick.

Mixed white-lead paint (pure or adulterated) will form an emulsion with its own bulk of water if run through the mill, and the water does not separate to any great degree, unless it stands for many weeks, and then being at the bottom of the can or package, escapes notice.

The covering or spreading power as well as the coloring power of such mixtures are of the poorest character; at least an extra coat and often two are necessary to present any sort of a creditable appearance. They dry solely by evaporation through the outer skin of the paint, leaving it porous, and where moisture can escape, the same element containing other atmospheric gases can enter and they are more destructive than the moisture they replace. All water-oil mixtures dry flat and lifeless. The use of alkalies and strong metallic-salt driers to form a better emulsion does not materially change their forced mechanical association, and if they cannot evaporate and escape outwardly, they go inward and condense on the covered surface, form blisters, and peeling results.

It is almost impossible to spread a water-oil paint in the cold without heating it. If spread and not dry, a cold night, not even approximating a frost, will ensure a blistering and peeling the next day. Brushing the coating over with turpentine or benzine will not prevent or correct this action, which will take place regardless of the nature of the pigment. A good linseed-oil paint spread on a cold day (not freezing weather) will "take" and dry if a little extra effort on the painter's part is made to brush it out well and by using a little more turpentine for the drier than that used in warmer weather. But all painting for external exposures should be suspended in cold weather, especially on all ferric structures, unless under cover and in a warm room, where the painted surface should remain until the paint has at least "*set*" firmly, or until it has dried enough to bear handling without feeling "tacky."

Many paint chemists deem that 2 per cent of water added to linseed-oil in excess of that natural to it, whether made from ripe or unripe linseed, is not detrimental to a paint. To enable the oil made from unripe seed to carry the extra water, it is rendered slightly alkaline, generally by adding lime-water, which forms with the oil vehicle a calcium soap that thickens the paint, so that it never settles hard, and is easily stirred up, consequently, does not *dry hard.*

A number of tests for free water in linseed-oil are: Heating the oil to 212° F. for a short time, and note the amount lost by evaporation. Filtration of the oil after heating and the addition of dehydrated copper sulphate, which turns bright blue when added to the oil. A strip of gelatine immersed in the paint for 10 or more hours will absorb the free water and swell up. Cool the paint or oil for a few hours in a refrigerator, and note the difference in its spreading. Heat a piece of iron to a bright cherry-red and plunge it into the oil or paint. If there is much snapping, it indicates the presence of free water in the mixture. In ordinarily pure oil or good paint, a thick, heavy smoke without explosion or snapping will follow the withdrawal of the glowing test-iron.

CHAPTER XXVI.

SUBSTITUTES FOR LINSEED-OIL.

Many so-called substitutes for linseed-oil have been presented to the public in the past, and at present they are numbered by the hundreds in the Patent-office records, and outside in the formulæ of the compounders of paints. All substitute oils are as uncertain and indefinite in character as the pigments assembled with them.

Generally, a low grade of linseed-oil is the base for the vehicle, to which one or more of the score of flax-dodders or buffums, resin, fish, mineral, india-rubber, and soap-fat oils are added. These are mixed with benzine for the volatile, also with manganese or other strong metallic-salt driers, put through the bung-hole. No heat is employed in their manufacture, and some of them are dangerous to sell, or spread even when cold.

Purchasing agents and master painters (except in a few cases) have not the laboratory, chemical apparatus, technical knowledge, or time to analyze them to detect the fraud. The result of their use comes with the lapse of a very short time, when the scraper, burning torch, and a new coating are the only remedies for the evils of crazing, peeling, or decomposition due to galvanic action. No amount of sophistry can change the fact that the use of so-called substitute oils has in nearly every case been detrimental to the paint and the covered surface.

Probably 80 per cent of all the oils, paints, and varnishes manufactured in the world is applied to structures of minor importance, which are destroyed by causes other than corrosion. These coatings are quite as much for looks as for physical condition, but the other 20 per cent is used on the most important and costly engineering structures of our time. These require protection from corrosion from the hour the materials leave the rolling-mill, forge, and foundry, until they are in the finished structure, and need more then than during construction.

Among the recent substitute or paint oils (dating from 1895) is the substance called "Lucol," for which extraordinary claims are made, viz.:

"Lucol"* is a paint oil, a *synthetical compound,* made by a secret process from materials that necessarily are a part of the manufacturer's secret."

What it is as a chemical compound, or as a manufactured paint oil, concerns the proprietors of it. What its claims are for superiority over linseed-oil, concerns the users. As set forth by its manufacturers, its characteristic features in comparison with linseed-oil are:

"1. Lucol is more durable than linseed-oil, which dries by absorption and oxidation and only to a small degree by evaporation. The reverse is the case with lucol, which dries principally by evaporation, hence the condition of the atmosphere to which it is exposed while drying must be considered.

"2. Lucol sets quicker than linseed-oil, which is the result of evaporation instead of the oxidation of its elements; the final drying to a bone-hard condition requires many months. The retention of its elasticity no doubt accounts for its durability.

"3. Lucol sets sooner and dries quicker than linseed-oil, hence is less adhesive for dust, and does not wash off if rained on, as is the case with other vehicles.

"4. Lucol gives a purer white with white lead than linseed-oil.

"5. Lucol preserves the original tint of the pigment longer. More lucol is used in a coating than when linseed-oil is used. The gloss is less at first than with linseed-oil, but it is soon ahead in this respect. The oil is the life of the paint.

"6. Lucol can be flatted with a much smaller proportion of turpentine than with linseed-oil."

Other advantages are set forth, but all are more adaptable for the use of lucol on surfaces other than ferric, and have been answered elsewhere in this work.

The Lucol Company says: "*We extract the olein,* which is carefully refined by a special and partly secret process, and by the use of chemicals it is converted into a brilliant, transparent, lemon-colored oil. It contains *no vegetable, mineral,* or *fish oil, resin or resin-oil, varnish-gums,* benzine, or other powerful solvent driers. Ignited it gives off an odor similar to that of burning india-rubber,

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* "Lucol." Excerpts from *Painting and Decorating Journal,* New York, February, 1895.

entirely different from the odor of linseed-oil in combustion. It has an unpleasant odor while being spread and in drying, wholly unlike linseed-oil, and should be flowed on similar to a varnish, instead of being brushed out like a linseed-oil coating.

"Lucol, in the form of a paint, resists alkaline substances, sea-air, sea-water, and covers galvanized-iron surfaces without peeling. Lucol weighs 7½ pounds per gallon, and is placed on the market on its merits as a *synthetical manufactured oil*, wholly unlike any other substitute compound heretofore offered as a paint-oil."

How well are the above claims founded? "We extract the olein," etc. This at once destroys the claim that lucol is a synthetical compound. It is only an oil made with a vegetable, an animal, or a fatty acid base.

All of the solid fats and oils are derived from two sources. The marine animal oils are obtained from the cold-blooded fish, like the cod, menhaden, etc., and the hot-blooded, like the seal, sperm, and right whale, etc. The terrestrial animal oils are lard, neat's-foot, horse-bone, tallow (oleic acid), etc. Both classes may be considered as mixed glycerides of oleic acid ($C_{18}H_{34}O_2$), stearic acid ($C_{18}H_{36}O_2$), and palmitic or benic acid ($C_{16}H_{32}O_2$); the first preponderating in the oils and the two last, especially the stearic (stearine), in the fats.

Oleic acid has a specific gravity of 0.808 at 65° F. and is the liquid acid obtained by the saponification of non-drying oils and liquid fats, which contain a different glyceride than the drying oils. The proportion of olein differs according to the nature of the fat from which it is obtained.

Chevreul prepared it by boiling human fat, lard, goose-fat, beef, and mutton suet, filtering the solution and allowing it to stand for 24 hours, then concentrating it a little by evaporation, adding water to separate the olein, and separating the liquid from the solid matter by pressure. Olein thus obtained does not solidify at 32° F.

Olein is also prepared from olive-oil and other glycerides containing it by pouring upon the fat a cold strong solution of caustic soda, which saponifies the solid fats but not the olein. It is also obtained from olive and almond-oils by treating them with cold alcohol and evaporating the solution.

Pure olein is a colorless oil void of taste and smell, insoluble in water, very soluble in absolute alcohol or ether. Specific gravity, 0.90 to 0.92; burns with a bright flame, oxidizes in the open air, yielding the same products as oleic acid. Crude, or carelessly prepared, the olein will have an odor distinctive of the class of fats from which it is obtained.

The marine oils all have the repulsive fishy odor in various degrees, sperm-oil being the hardest to locate. The terrestrial animal oils have the peculiar sourish odor of cooking fats. The vegetable oils have a sweetish odor. A little practice with a heated sample will enable the most of them to be recognized.

Olein is also extracted from the organic acids in soap-stock or the fats left in the by-products in the refining of cottonseed-oil. The fatty acids in the "foots" are distilled with superheated steam; when the distillate cools and solidifies, the olein is extracted by pressure. The process is analagous to the production of commercial cottonseed-oil and lard stearins used in the preparation of butterine, lard surrogates, and candles. There are about 250,000 gallons of olein available in the cotton crop of the United States, if all the foots were used for the extraction of olein and none used for the manufacture of cheap soaps.

There is no amount of animal oils or fatty refuse available for manufacturing into olein that can in any material way affect the broad field covered by linseed-oil as a vehicle for paints.

Chemistry has not arrived at that stage of development where the assembling of the chemical elements of fatty substances in their known proportions will produce an oil or fat. All such substances must have a natural base for the foundation for the chain of operations and reactions necessary to change their nature.

Lucol, as a paint vehicle, therefore, is not a synthetical compound, but a manufactured paint oil. Its endorsement by master painters when used on passenger-cars or other works which are covered by coatings of fossil-gum varnish, or upon ferric bodies which are thoroughly covered with rust, is no evidence of its resistance to corrosion. A few successful applications of it under favorable conditions will not counterbalance the failures. Generally, no record of the failures of substitutes for linseed-oil is available for the public, who are as much interested in knowing what not to use, as what vehicle is the best for a paint.

A siccative oil of peculiar properties has lately been introduced from China into England and the United States. Its comparison with linseed-oil for paint and varnish coatings is as follows:

Chinese wood-oil * has thus far been employed for the manufacture

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* "Uses of Chinese Wood-oil in the Manufacture of Paints and Varnishes." Translated from the *Färben Zeitung,* by the *Scientific American,* January, 1895.

of lacquers, varnishes, and paints, on account of its peculiar quality of drying thoroughly in about 6 to 8 hours. Pigments ground in the oil furnish excellent paints, that do not remain soft and sticky below the surface, like coatings prepared from linseed-oil.

Chinese wood-oil is favorably employed as a floor oil or paint on account of its hardness; also in the manufacture of an oilcloth-like goods, which, when dried in hot air, excel the ordinary oilcloth or water-proof products by their extraordinary elasticity. The odor of the oil is very peculiar, resembling lard, and remains in the coating for months, and even for years. This lard odor remains in the lacquers made from the oil; hence for that use, also for floor and other interior uses, it is necessary to remove it. Disguising the smell by the use of a volatile oil does not answer the purpose, because the odor reappears after the evaporation of it. Among the remedies resorted to are: Agitation with a dilute solution of permanganate of potassium; a filtered solution of chloride of lime, filtration through animal charcoal; mixing with potato flour, also storing it for a long time after filtration, after the process of Bang and Ruffin. It is also possible to obtain a tolerable freedom from the odor by the use of a blower passing air heated to *not exceeding* 50° C. through the oil, for 6 to 8 hours, when it loses perceptibly in odor and can be used for lacquers or floor-work. For outside exposures it is not necessary to attach much value to the deodorization.

Wood-oil in its raw state dries opaque, probably due to the presence of mucilage and albumin. In this state the oil becomes waxy at low temperatures, and organic salts analogous to the stearates settle out.

Wood-oil is boiled for a short time in a like manner to linseed-oil with a small percentage of red lead or litharge, else it will always remain opaque. This for paints is immaterial, but boiling is necessary to give a greater drying quality.

In boiling the oil, whether with lead or manganic compounds, a temperature of 200° C. must not be exceeded, otherwise, in the use of borate of manganese, a thickening ensues, followed in a short time by complete gelatination and waste of the oil. Heats approximating 160° C. and in any case not over 180° C. should only be used, and for but a short time, when the oil should be removed from the fire and the siccatives stirred in. This imparts to the oil a drying quality and obviates gelatination. Pigments can be ground in the oil as usual with the use of linseed-oil. Compositions of linseed-oil and wood-oil work well together, being especially adapted for exterior varnishes on account of the hardness, solidity and quick drying they receive from the wood-oil, and the elasticity from the linseed-oil.

The important drying quality renders wood-oil useful in the manufacture of fatty lacquers. It cannot be employed for spirit lacquers, as it is insoluble in alcohol.

The wood-oil of China and Japan is obtained from the seeds of the tung-oil or varnish tree (*Aleurites cordata, Elaeococca vernicia*). Another variety, the *Aleurita triloba,* furnishes an oil of less drying power, and is used to adulterate the oil from the former.

About 266,700,000 pounds of the oil are annually shipped from Hankow to other parts of China, and for export. The Canton wood-oil is said to be better and purer than the Hankow, and is about 10 per cent higher in price. The cost of these oils in England, where their use is firmly established, is from 4 to 4½ cents per pound.

De Negri and Sburlati report that the fruit of the tree from which the oil is extracted contains 53.35 per cent of oil, 42 per cent being recoverable.

The cold-pressed oil is of a pale-yellow color, is tasteless, and has a smell like castor-oil. The hot-pressed oil is a medium brown in color, with a taste and smell like hog fat.

The drying power of the oil is superior to that of linseed-oil, the cold-pressed drying better than the hot-pressed.

Its specific gravity is 0.936 to 0.941. Saponification value, 156.6–172. Iodine value, 159–161 (de Negri and Sburlati). The oil is soluble in cold absolute alcohol and mixes readily with linseed-oil. When heated with litharge it turns darker in color and evolves a slight smell of acrolein. When thinly spread on glass in a closed room it dries to a whitish film resembling milky or frosted glass. A heavier coating exposed in the open air dries in about 6 hours. The oil after heating or boiling by itself develops the whitish film, but when boiled with litharge is as clear and bright as any oil varnish.

Very thick layers of the dried oil can be scraped off as a tough mass quite uniform throughout. It has an exceptionally small adherence to glass.

The balsam known as wood-oil or gurjan balsam, from the *Dipterocarpus turbinatus, Gaertn,* should not be confounded with the tung-oils. It is frequently adulterated by them. It is also a natural varnish.

Euphorbium.

This substance is in its experimental stage in the United States as a vehicle for anti-corrosive and anti-fouling paints. Attention was directed to its anti-corrosive qualities as a natural varnish and its probable utility as a vehicle for paints about the year 1870, from the discovery that the axes, machetes, and other tools used to cut down the thickets of the euphorbia spurge, to clear the way for a surveying expedition in Natal, became coated with a strong glutinous juice that adhered so firmly to them as to be with difficulty removed. The tools coated with it did not rust in fresh water, and bilge-water had but little effect upon it. When articles were coated with it and immersed in the sea, no barnacles or marine life would adhere to it. Its effect upon insect life appeared to be equally repulsive, and timber coated with it resisted the ravages of the *Teredo navalis*. It resists heat and cold better than linseed-oil and varnish vehicles, while ammoniacal and chemical vapors do not cause blistering, scaling, or other injurious action.

Euphorbium juice has a strong affinity for iron and steel, and when applied in its crude state as it exudes from the shrub, has no injurious effect upon metals, wood, or other substances used for engineering or common building purposes. When prepared for a paint, the juice undergoes several special processes and becomes a clear gummy vehicle of a medium-brown color, that receives the usual color pigments much as linseed-oil does; retaining, however, its own protective properties unimpaired.

Euphorbium, prepared for a vehicle, appears to maintain its properties in all climates, and does not apparently deteriorate with age. It is perfectly elastic, tenacious, and when dry, can be drawn out to a thin thread. It adheres firmly to polished steel, tin plate, zinc coatings, sheet lead, and spelter. Earth acids appear to have little effect upon it, as pipes coated with it and buried for a number of years show little injury.

Euphorbium juice has a bitter, biting taste, is very acrid and irritating to human flesh, corroding and ulcerating the body wherever it is applied. The sores resemble those from nitric acid, and are hard to heal. In this and nearly all other respects it resembles the crude juice gathered from the *Rhus vernicifera*, called by the Japanese *urushi-naki*, the native lacquer-tree of Japan.

The euphorbium of commerce is imported in casks, and is a gummy, resinous substance in the form of drops of an irregular size resembling gum arabic. The drops contain vegetable matter—twigs, flowers, thorns, etc., that collect on the gum as it exudes from the tree and are dried in; though many of the tears are hollow and without refuse in them. The natural color of the tears is a cloudy pale yellow externally, but of a lighter color internally. The tears break easily in the fingers, but are difficult to pulverize. The principal part of the process to prepare the crude gum for use as a varnish or a vehicle for paint is to free it from the vegetable matter. It is partially dissolved by water and almost entirely by alcohol, ether, and oil of turpentine. Its composition by analysis is, viz.:

A resin soluble in ether	26.95	per cent.
“ “ insoluble “ “	14.25	“ “
Euphorbin, the peculiar principle	34.60	“ “
Caoutchouc	1.10	“ “
Malic acids	1.50	“ “
Gum salts	20.40	“ “
Ammonia soluble matters	1.20	“ “
	100.00	“ “

It has no acid reaction but an extremely burning taste.

The intense acridity is due to the resin, soluble in the ether, which melts at 107.6° to 109.4° F. The resin insoluble in ether melts between 246.4° and 248° F. Euphorbin is a crystallizable substance, fusing at 154.4° F., and soluble in ether, benzine, etc., but not in hot water.

Euphorbium dries readily without the use of metallic salts or solvent driers. Ox-gall and other kindred substances appear to be the best driers for it, when any are required. The crude resin is the product of the *Euphorbiaceæ:* the genus is numerous. There are about 600 species, many of which are natives of nearly every country in the temperate zones, and are commonly known as spurgeworts.

The euphorbium spurge, or *E. resinifera,* is a shrubby and herbaceous succulent, frequently covered with thorns and having stalks from 3 to 6 and sometimes 10 feet in height, and grows in almost impenetrable thickets in the hot interior deserts of Morocco and other hot climates. Euphorbium is obtained from the incisions made on the plant; the corrosive milky liquid hardens on the stems in resinous drops or tears, or like spruce-gum deposits, and is collected in various ways.

The commercial supply comes principally from the southern provinces of Morocco, in the districts of Aitaitab and Juteefa, at the foot of the lower range of the Atlas Mountains.

The euphorbium gum from Natal is considered to be inferior to the Morocco product. North Africa is capable of producing euphorbium in sufficient amounts to supply almost any demand for it.

The gum is called in Arabia "Darkmows," and is known in the Eastern markets as "Farfium."

In India there are 116 species of the *Anacardiaceæ* referred to 23 genera, in addition to the *E. resinifera* and some other varieties found in Arabia.

The *E. dracunculoides* in India (*jy-chee*) yields 25 per cent of a clear oil of a yellowish or greenish-yellow color from the dry husked seed. The oil is more limpid than linseed-oil, does not become ropy from age, and is used for a burning and drying oil.

The *E. lathyris* is raised on the edges of the fields in France, Germany, and Switzerland. It contains 40 per cent of a fluid oil of a siccative nature.

The *E. neriifolia* grows wild in Burma, Baluchistan, the Malay Islands, etc. It yields a gum of a gutta-percha nature on boiling the stems and twigs of the shrub.

The *E. Royleana* is a large fleshy shrub common on the dry rocky hillsides of the Himalayas, growing at an elevation of 6000 feet. The sap of this plant yields a superior gutta-percha.

The *Pisticia Lentiscus* yields the resin mastic.

The *Melanorshœa usitatissima* yields the black varnish of Burma.

The Indian *Holigarna longifolia* also yields a varnish.

The Indian *Odina Wodier* is covered with its brown gum, which streaks down the stem and ultimately turns black.

The *E. pulcherrima* is an ornamental shrub grown in Mexico that yields a milky sap which hardens into a black gum, and can be boiled down to a sort of gutta-percha. Guatemala and other countries near the torrid zone also have a large number of trees that furnish the natural varnishes, though no attempt has been made to bring them into commercial importance.

The *P. terebinthus* is a tree growing along the shores of the Mediterranean Sea. It furnishes the cyprus turpentine.

The Japanese lacquer-tree, or the *urushi-naki*, is known in China as the *Tsi-chou*. It belongs to the botanical order of *Anacardiaceæ*, to which also belongs the *Rhus vernicifera*, a tree with very long, glossy leaves resembling those of the ordinary sumach, poison-oak, dogwood, ivy, etc. The American dogwood was formerly thought to be of the same species, but is now placed in another of the same order.

In Japan * the lacquer-tree grows to the height of about 30 feet, and at the age of 40 years is about 40 inches in diameter. It reaches its greatest perfection in the yield and quality of the lac or varnish at the age of 18 years.

The crude lac, called *ki-urushi,* is collected at any time between the months of April and October by making a number of horizontal incisions in the bark of the tree in a manner similar to the "boxing" practised to gather the sap of the long-leaf pine- or turpentine-tree. The tree is hacked in this manner for from 60 to 80 days, or until it dies, when it is cut down, the bark and sap-wood removed and steeped in hot water, which extracts the last remnant of the lac, about half a pint, which forms the poorest quality of lac, known as "*roiro-urushi,*" or black varnish. The tree seldom survives the first season's hacking, at whatever age it is done.

The varnish-tree is probably native to China, but it is also found native in Japan, and is cultivated all over Nippon and in several districts of Kiushia and Shikoku, and there are extensive plantations in the valley of Tadamigawa and Northern Echigo. A temperate climate seems to best suit the growth of the tree, as it reaches its greatest perfection on the main island north of latitude 36°. It is cultivated in Northern Hondo, between 37° and 39°. It may be of interest in considering the question of habitat to note that the *Rhus vernicifera,* mentioned by Mr. J. J. Rein, are growing in Germany at Frankfort-on-Main and at Strasburg. They endured the hard winter of 1879–80, when the temperature reached 27° C. In Japan the lowest temperature in Northern Nonshiu is $-12°$ C.

The lac is purified by straining it through cotton cloth, evaporating the water by exposure to the sun or by a gentle heat. Sometimes water is added to the crude lac, and they are ground together on a paint slab, and then the water is evaporated. Various coloring matters are added to the purified lac by grinding, as is usual in the manufacture of oil paints. Black lacquer other than that furnished from the last run of sap is produced by the addition of some salt of iron.

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* Excerpts from "Japanese Lacquer and the Varnish-tree that produces it." A communication to the author from the Bureau of Forestry, United States Department of Agriculture. By Geo. B. Ludworth, Chief of Division of Forestry Investigation, June, 1902.

Whenever driers are required, a little oil of tea is used, also the gall from pigs and oxen, to give body to the lac. The purest lac is from the first run of the sap after tapping. It is called *nashyi-urushi*, and is bleached in shallow vessels laid in the sunlight. The other principal grades are the *henki-urushi*, the unbleached *jeshimi-urushi*, and the *roiro-urushi*, or black varnish.

There are about 20 different grades and qualities of these lacquers in the Japanese market, of which the above are the principal ones. They vary in color from a light brown to a deep jetty black.

Lacquer is thinned only by heating. The addition of water thickens the lac into a jelly. Lacquered objects are always hardened in a humid atmosphere, such as a room with wet cloths hung on the walls, or containing a spray or vessels of water.

All varieties of varnish-trees are propagated by the seeds and cuttings. The seeds are gathered in October and sown early in the spring, make 10 to 12 inches' growth the first season, and in 10 years are 9 to 10 feet high and from 2 to 3 inches in diameter. In a favorable soil the annual height-growth during the first 6 years is from 20 to 30 inches, and diminishes afterward to from 10 to 20 inches. Plants from root cuttings grow more rapidly than seedlings, but the latter make hardier and longer-lived trees. The trees after the first 5 or 6 years require very little care, and are generally tapped at any period after the tenth year of their growth, though sometimes it is done when only 4 or 5 years old.

The climate and soil of at least one-third of the United States are as favorable for the growth of lacquer-trees as those of Japan or China. Their cultivation requires no more care than that given to the sugar-maple or the Eucalyptus. Specimens of the trees are growing in the grounds of the Department of Agriculture at Washington, D. C.

Plants which are largely cultivated in Europe have been confused with the Japanese *Rhus vernicifera*. They are, however, a different variety of the tree. The *Ailanthus glandulosa Desf.*, in France called *Vernis de Japan*, is also of the varnish-bearing species.

The poison-sumach, *Rhus verneata*, common in the Eastern United States, yields a sap that furnishes a black, lustrous, durable varnish, very similar to that derived from the Japanese tree.

Other trees that belong to the same botanical order (*Anacardiaceæ*) that yield natural varnishes have been referred to in the article

"Euphorbium." None of the Indian varnish-trees west of the Ganges yield as white or pure a lacquer as those in China or Japan.

A species of varnish-tree that grows in India was thought to be the veritable *Anacarde,* but it is entirely different from the Japanese "*urusi*" variety.

No attempt to cultivate any of the varnish-trees on a commercial scale has been made in either Europe or America. The manufacture of lacquer and lacquer-ware is one of the most important industries of China and Japan. It seems natural that if the largest users of varnish in the world depend almost solely upon these natural products, their cultivation in America is well worth trying.

In China the *Rhus vernicifera,* or varnish-tree, is called *Ch'i-shu* (*Tsi-chou*), also *Li-tschi.* It grows wild in the province of Fingo and on the island of Tricom, and is cultivated in the mountains of Hupeh and Seechwan, but the best varieties are found in the province of Jamatto, where it is cultivated extensively. It is probable that the Mingpo and Foochow varnishes, as well as the Hupeh, are from the *Rhus vernicifera* A varnish-tree growing in South China differs from the above variety, but is not well known at present.

In China the *Rhus vernicifera* grows about 15 to 20 feet in height, seldom reaching one foot in diameter, and has but few branches. The bark is white, knotty, and peels readily. The wood is fragile, resembling the willow; the pith is very abundant. Its leaves have a mild taste, and when rubbed on paper, dye it a dull black. The flowers are greenish yellow, and have an odor resembling orange-blossoms. The fruit is of the size and shape of chick-pea, and at its maturity is very hard and of a dirty color. The seed furnishes an oil and wax which are extensively used.

From the berries of the *Rhus vernicifera, Rhus succedaba,* and other related Chinese and Japanese species, a vegetable tallow is extracted and used for candles. The wax is exported in large quantities to Great Britain and the United States for an adulterant or substitute for beeswax.

The general composition of crude lac is lac acid (a resinous acid, soluble in ether), 60 to 80 per cent, a gum 3 to 6 per cent, a nitrogeneous substance resembling albumin 1.7 to 3.5 per cent of a volatile acid, and water, which are driven off in the preparation of refined lacquer. The color of the lacquer is a light yellow or brown, according to the season in which the tree is tapped.

The Chinese crude lac is collected and purified in the same way as in Japan. In both of the processes for its collection and refining great care is necessary. The poisonous element in the lac, whether inhaled or in contact with the flesh, produces what are known as varnish boils, accompanied by an intolerable itching and burning sensation, similar to that produced by the poison-ivy. They are difficult to heal, and resemble the effect of nitric acid on the flesh.

The Chinese and Japanese use lacquer as a varnish or vehicle for colors on all kinds of household utensils, also for the inside and outside coatings on their buildings. Lacquer as a vehicle can be used for all colors except a pure white and some of the lighter shades of other colors. It is applied to wood, porcelain, and metals, and forms a hard resinous surface, highly lustrous, practically insoluble in boiling water, alcoholic liquids, alkaline and acid solutions, unless in a highly concentrated form. Applications of lacquer to the under-water surfaces of a number of Japanese war vessels for both anti-corrosive and anti-fouling coatings have been very successful. The coatings, after a sea-duty of four years of the vessels to which they were applied, showed no signs of either fouling or corrosion. Applications of other anti-fouling paints of all characters over lacquer coatings were failures, the *urushic acid* of the lacquer attacking the metallic base of the foreign anti-fouling paint, resulting practically in the destruction of both.

The best results for under-water marine work with lacquer is had when the first coating is a heavy one and almost pure lacquer. The succeeding coats can be thinner in body and contain either a pigment or some inert substance to give body. Mica, graphite, lampblack, etc., have been used experimentally with success for these secondary coatings.

CHAPTER XXVII.

DECAY OF PAINT.

Rust proceeds solely from the action of an acidulated moisture upon a bright or clean iron surface, and is probably only a point at its inaugural. The affinity of the iron for the oxygen in the acidulated moisture of the air or water in the oil, or from other sources, is greater than its bond with the hydrogen as water (H_2O), the decomposition ensuing releases the hydrogen, which is sixteen times the volume of oxygen united with the iron to form hydrated Fe_2O_3 or red rust. The hydrogen, from its light specific gravity, in its effort to escape into the air pushes up the overlying paint coating, increases the area of the affected part, cracks the coating in its exit, moisture enters again, and corrosion is master of that location. The rust which has thus been formed is hygroscopic and carries 24 per cent of moisture as it forms. This moisture *never dries out* under any atmospheric heat conditions, but is ever ready for a chemical decomposition; the hydrated red rust, being nearly two times the volume of the iron from which it is formed, adds its efforts to the free hydrogen to push up the coating and form a blister and crack in the coating. How energetic this mechanical action due to corrosion is, may be observed on the ordinary cast-iron hand railings for fences and outside steps of New York City and other city houses, which in hundreds of instances are split for more or less of their length. Cast-iron water or gas-pipes, with bell and spigot joints, are frequently made with rust joints. They almost invariably burst the bells by the swelling of the iron cement used to make the joint.

The cut, Fig. 35, shows a section of a well-known railway viaduct, the iron construction having been painted over mill-scale, or in the condition the material left the rolling-mill and workshop. It had received the usual treatment given by contracting engineers to remove the mill-scale preliminary to painting.

Many sections of the New York City and other elevated railways, also the Brooklyn Suspension Bridge trusses show mill-scale corrosion to an equal extent. Fig. 36 shows the mill-scale corrosion on one of hundreds of New York elevated railway columns, originally painted with red lead. The corrosion now in progress is strong enough to break through and cast off six or more paint coat-

Fig. 35.

Fig. 36.—Mill-scale corrosion, Phœnix column.

ings that have been applied over the red lead since the columns were placed in position.

The corrosion existing in Brunell's* tubular iron bridge over the St. Lawrence River at Montreal, Canada, had proceeded to so great an extent as to require the removal of the whole structure, it being impossible to repair it. The efforts to replace the cross floor-beams supporting the rail stringers resulted in loosening every rivet in the neighborhood of the repairs. Pitting around the heads of the rivets had proceeded so far and deep that it was impossible to cut them out without loosening every contiguous rivet.

This bridge had been kept well painted with iron-oxide and some experimental paints applied coat after coat. These coatings whenever removed, or that fell off during the periodical clean-up, or attempts to repair and paint the structure, showed the several coatings of mill-scale, paint, and new rust formations as plainly arranged as the leaves of a book.

Fig. 37 shows a similar state of corrosion.

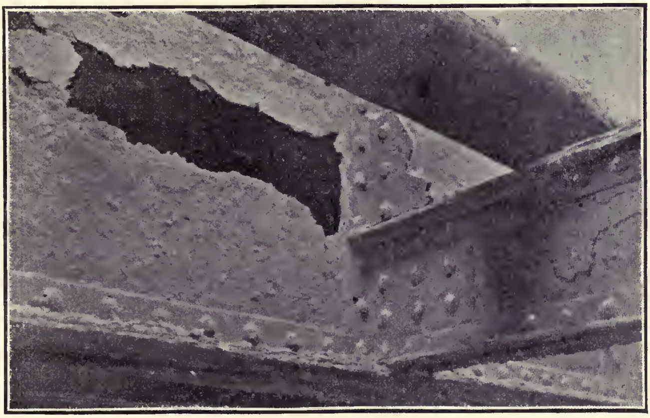

Fig. 37.—Corrosion of steel girder, Washington Street railway bridge, Boston, Mass.

In 1879, Sir Nathan Barnaby stated as the result of his observations of ships' metal in the English naval stations, that when the mill-scale was left upon the plates, angles, and other parts of the ship, its effect upon the neighboring bared metal was as strong and continuous as copper would be.

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* Transactions American Society Mechanical Engineers, Vol. XV, 1894, paper number 626, p. 410.

In 1887, Mr. Rialton Dixon gave before the Institute of Naval Architects his experience as to a vessel built entirely of steel some eight years before, which was found to be greatly corroded in the bunkers and water-ballast chambers near the engine room and boilers. Some of the angle-irons had entirely disappeared, and the tie-plates were eaten away in holes. This action could be traced directly to the presence of mill-scale, and whether the surfaces were coated with paint or cement or not; the corrosion was always present upon those plates and angles that had mill-scale upon them, and *was absent* in those free from it. The presence of the paint or other coating retarded corrosion only in a minor degree by preventing moisture from reaching the metal covered by the mill-scale.

In 1882 Mr. Farquharson, on behalf of the English Board of Admiralty, conducted a number of very exhaustive experiments at the different naval stations to test the action of mill-scale on ships' metal. The result was to establish beyond dispute that, first, no pitting occurred on mild steel *when freed from mill-scale;* second, that the loss in weight from corrosion of clean mild steel and clean iron did not differ much; third, that the action of mill-scale is considerable and *continuous, and equal to a similar amount of copper in its corrosive action* on metal covered by it. Since these experiments the Admiralty have never wavered in their practice of having all of the ships' metal pickled to remove the mill-scale, whether it is to be covered by paint or cement, or to be galvanized.

Destructive Agents of Paints.

Pure water is a greater destructive element to an oil coating than solutions of sal ammoniac, chloride of magnesium, common salt, or natural sea-water, if free from sewage, all of which are agents of destruction. The decay of a paint is hastened by mechanical action if the water, either fresh or salt, or the other solutions, are in motion. Ordinary commercial oil coatings are destroyed by diluted muriatic and nitric acids, alkaline liquors, ammonia, sulphide of ammonium, soda, caustic alkalies, and alkaline solutions of coal ashes, clinkers, cinders, soot, etc. Diluted sulphuric acid *does not* materially affect an oil coating. All gaseous acids destroy the coating quicker than the acids in diluted aqueous solution, the destruction being in all cases hastened by heat or motion. Hence, to determine the probable protective value of any paint or other coating, it is necessary to know the detrimental influences to which it is to be subjected.

Changes in Paint Coatings.

A coating of paint appears to be a very simple thing, as it is, when applied to a house or barn and both are left to their fate, but when applied to an important engineering structure, with all the vicissitudes of service in the extremes of heat and cold, sunshine and storm, atmospheric and other gases from natural or manufacturing sources, from corrosive liquids and solids, it is a different matter, and requires more engineering experience to select, more chemical knowledge to compound, and more technical details to get the right thing in the right place at the right time, in the right manner, and in the right amount than the general run of master painters do or can give to the subject. If the influences to which a coating of paint is to be subjected are known, it can generally be determined in advance whether it will be durable. For instance, zinc white or oxide (ZnO, specific gravity, 5.42) applied as an external coating absorbs carbonic acid from the air and some moisture, changing to a carbonate of zinc ($ZnCO_3$, specific gravity, 4.44). During this change there is an increase in volume from 14.9, as an oxide, to 28.1 as a carbonate. This change from an oxide to a carbonate is a chemical one, and occurs during the process of drying, but the *change in the volume* of the two substances exerts a mechanical action also in the atoms of the pigment, not only to disrupt them and leave them loose and easily carried away by the wind, rain, etc., but cracks and loosens the oil vehicle in which the pigment is embedded as well as its bond to whatever surface it covers But if the zinc-oxide coating is applied in a closed room, though the air contains the same amount of carbonic acid, or even more than the external air, the oxide does not change to a carbonate, as the necessary moisture is lacking; hence zinc oxide for internal coatings is durable, but for outside coatings is perishable.

Red lead (Pb_3O_4, specific gravity, 9.07) remains unchanged under ordinary atmospheric conditions, but if the air contains hydric sulphide, as it does in many manufacturing establishments and towns, to a notable extent, it will by an inexorable chemical law change the oxide to a sulphide of lead (PbS, specific gravity, 7.13), and this chemical change (usually denoted by the blackening or discoloration of the coat) will also be accompanied by an increase in volume of the sulphide of about 22 per cent, this increase acting mechanically to disturb the bond between the pigment vehicle and surface coated.

The addition of carbonate of lime (chalk) to an iron-oxide pigment, whether made from the iron ore, or from calcined copperas ($FeSO_47H_2O$), to neutralize the sulphuric acid developed in the calcination of the copperas or roasting of the ore (as heretofore noted), is another instance in which an inexorable chemical change in one of the pigment's loose substances is accompanied by a change in its specific gravity, its corresponding change in volume, and a mechanical action to reinforce the chemical action due to the raw-oil vehicle loaded with its charge of driers, whose function is to either decompose or consume by a slow combustion the "*mucosities*" in the oil while attempting to dry. All these instances are similar in effect to what would occur in the plastered wall of a building if the mortar used in it, when partially dry, should begin to increase in volume to the amounts as given above. Other instances could be cited, but these show that the pigments of the coating can be so chosen as to preclude the destruction by them of the coating, but that it is almost impossible to guard the vehicle from the injurious influences inherent in the composition of the pigment, that is changed in character, after its application, by chemical laws. Hence the absolute necessity that an order for a protective paint should include the conditions it is to be subjected to.

In addition to the preceding remarks upon iron oxide, graphite, and other paints, and the several tests given in detail of a few of the many paint compounds, it may be noted, viz.:

All pigments * can be grouped into three classes, according to their affinity for linseed-oil.

First. Those that form chemical combinations called soaps and are generally the most durable. They consist of lead, zinc, and iron bases, of which red lead combines with the oil to the greatest extent; next, the pure carbonate white lead made by the "Old Dutch Process," followed by zinc oxide and iron oxide, Turkey umber, yellow ochre; also, faintly, the chromates of lead, chrome-green, and chrome-yellow.

Second. Pigments of this class, being neutral, have no chemical affinity for the oil; they need large amounts of driers, either combined with and carried by the oil, or as free driers. They include all blacks, graphites, slates, slags, vermilions, Prussian, Paris, and Chinese blues, terra de sienna, Vandyke brown, Paris green, verdigris, ultramarine, carmine, and madder lakes. The last seven are trans-

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* "Pigments." English Encyclopedia of Painting, 1880.

parent colors, and are better adapted for varnish mixtures and glazing.

Third. Pigments of this class act destructively to linseed-oil. They have an acid base (mostly tin salt, hydrochloride of tin, and redwood dye) which forms, with the albuminous and gelatinous matters in the oil, a jelly-like compound that does not work well under the brush nor harden sufficiently, and can be used in a varnish for glazing only. Among the most troublesome are the lower grades of so-called carmines, madder lakes, rose-pinks, etc., which contain more or less acidulous dyes, forming with linseed-oil a soft paint, that dries on the surface only and can be peeled off like the skin of ripe fruit.

"Catalysis" is a term introduced by Berzelius, and by him applied to the changes that sugar solutions undergo in the process of fermentation, and now used to denote the changes that certain substances, by their mere presence, effect in other bodies without themselves undergoing any apparent change. Catalytic action is a potential agent in the decay of paint coatings, and manifestly has not received the attention from paint chemists and compounders that its marked action on the life of a coating warrants. The present efficiency of the incandescent gaslight is wholly due to catalytic action between the substances that compose the mantle when excited by the combustion of the gas. In the development of this light all of the rare mineral oxides and metals and the oxides of the baser metals, chromium, alumina, cobalt, manganese, nickel, and iron, when associated with thoria in the mantle, have been found to act as catalytic agents to carry, condense, or absorb oxygen, that increases the flame temperature of the mantle and consequently increases the light. This flame temperature in some cases reaches the point where volatilization of some of the baser metals and oxides ensues. Charcoal, powdered glass, porcelain, flour spar, crystallized quartz, pumice-stone, and other kindred substances are also found to act as catalytic agents in combustion, but do not develop so high a flame temperature in the mantle as the other substances above noted.

Combustion of any substance may be quick and attended by a high temperature, as in the case of the incandescent gaslight, or it may be of low temperature and extend over years of time, but the amount of heat evolved from the destruction of the substance and the resultant products of combustion, or decomposition, are the same in all cases, even if the physical effects are apparently different.

Nearly every substance in a paint coating has been found to be catalytic to some other substance, either in its own class as a so-called inert mineral pigment, or in the chemical class of oxides having a lead, zinc, iron, or other metallic base. Individually, they may be apparently unaffected by long exposure to the air while in their loose state or in packages or bulk; but when mixed together, they take up moisture or oxygen to a greater or less degree, either by absorption in mass or by condensation upon their surfaces, and catalytic action ensues. The oil vehicle and driers are catalytic of themselves, and when mixed with the pigments act more energetically as carriers of oxygen even when the coating is apparently dry. In all pigments and vehicles, the one that is the most refractory, or that is the most resistant to oxidation in whatever form the oxygen may be presented, is the one that acts the part of the thoria in the gaslight mantle, becoming the negative or non-consumable substance, that, though excited to a greater activity by the presence of the other substances in the paint compound, retains its resistance to a change the longest at the expense of the other associated substances. Thus far, lampblack and graphite, in their subdivided form as pigments, appear to be the only substances not subject to catalytic action, or if it is present it is so weak that the life of the coating is not materially affected from this cause.*

Caustic Action of Mortar upon Paint.

An examination (1901) of iron floor-beams taken out after an exposure of about forty years showed that the beams originally were particularly well painted and laid in a location where only the dry warm atmosphere of a residence reached them. The paint coatings had been thoroughly destroyed by the caustic action of the lime mortar used to turn the brick arches in which the beams were embedded. Corrosion was well established in every inch of their surface. Had any moisture, as in the case of the Times building, reached them, their condition would have been fully as bad.

The iron beams supporting the sidewalks laid about forty years ago in New York City, that were removed for the Rapid Transit Tunnel work, invariably show deep corrosion from the destruction of the paint coatings from the caustic action of the lime mortar,

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* A full list of the series of electro-chemical elements having a metallic base and entering into the composition of pigments is given in Chapter XXXVI.

also, that the dried mortar *is not* a protection from corrosion, but a promoter of it, if moisture or air can reach the surface so covered.

FIG. 38.—Corrosion of sidewalk iron beams.

Hydraulic, also quicklime mortar, only prevent corrosion so far as they are free from mill-scale and continuously dry to exclude the air. The paint coating when burned by the caustic action of mortar or cement, adds no material period to the life of the iron and except for appearance and protection during construction, might be left off. (See Chapter XV.)

The modern hollow tiles used for floor arches and building partitions with their advantages over brickwork, do not remove the cause of the corrosion of any iron that they may be in contact with.

Gypsum, while not caustic, is hydrometic, and the continual presence of moisture is fatal to ferric bodies; besides, it is not always free from caustic substances developed in the calcination of it.

The following cement for the levelling, bedding, and in contact with metal work, is recommended. The cement hardens like stone, is impervious to water, and can be applied by a trowel from a mortar-board, over walls or to lay brick wherever mortar can be used. It is made from marble dust (from marble sawing or pulverizing mills) mixed, viz.:

Pulverized marble..............	62 per cent.
Sharp silicious clean sand........	35 " "
Litharge........................	3 " "

These proportions can be varied somewhat without injury. Too much limestone impairs the hardness; too much sand makes the cement porous. When the mastic is to be used, for every 100 parts of such mixture, 7 parts of linseed-oil are required to bring it to a good trowel paste. The oil can be either raw or boiled, according to the time of drying required. The surfaces to which it is to be applied should be dry, clean, and preferably coated with linseed-oil or a good carbon paint, before the application of the cement.

A refined bitumen coating applied to the bright metal, hot, has proven to be the best of coatings for ironwork laid in cement, mortar, or concrete, to correct the caustic action of them.

The metal work of the movable dam at Lake Wennibioskish, Minn., constructed in 1899–1900, was cleaned bright by the sandblast and then painted three coats of Edward Smith's Co.'s Durable Paint, applied one week apart, each coating being thoroughly dry before the application of the next. Observation of the paint in 1901 showed that the coatings had been completely killed and absorbed wherever the painted metal was embedded in the concrete. The metal was as clean as before painting, with a slight discoloration of the surface of the concrete from the paint absorbed. The metal exposed, however, did not show the same tendency to rust quickly, as before the application of the paint, on the short exposure before again being put in place. The surfaces not in contact with concrete were in good condition.

CHAPTER XXVIII.

SAND-BLAST AND PICKLING PROCESSES.

THE sand-blast is the most satisfactory and simplest method of cleaning all surfaces for painting, whether at the shops or *in situ.*

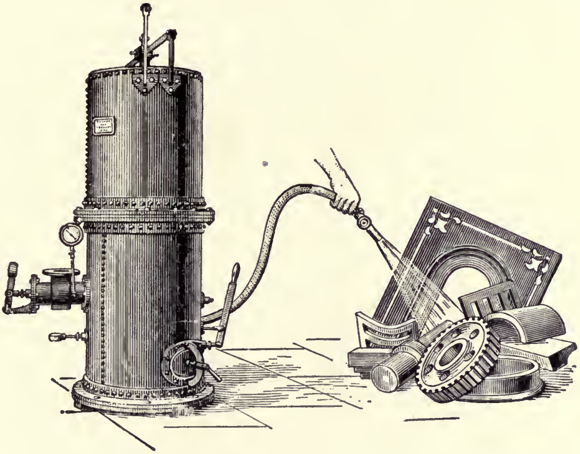

FIG. 39.—Sand-blast apparatus.

The invention of the sand-blast is due to General Benj. Tilghman, and was patented October 18, 1870, No. 108,408, but has since expired. There are some patents for sand-blast apparatus of subsequent date, issued to other parties for improvements relative to portability, clogging of the sand in the case, etc., still in effect.

Fig. 40 shows a portable sand-blast apparatus used by Mr. Geo. W. Lilly, C.E., for cleaning railway viaducts in the city of Columbus, Ohio.

The principal features of the sand-blast consist in the use of compressed air at a pressure of from 15 to 25 pounds per square inch, discharged through one or more chilled-iron or hardened-steel nozzles $\frac{9}{16}$ inch in diameter, which are directed upon the work to be cleaned. By suitable devices, into this current of air, dry sharp sand or coarsely powdered quartz is fed at the rate of about 10 cubic feet per hour for each nozzle, which discharges about 120 cubic feet of free air per hour, or about 1 cubic foot of sand to 1000 cubic feet of free air per hour. The nozzles wear rapidly and require frequent renewal, but they are of small or minor expense. The 2 or 2¼-inch diameter armor-clad rubber hose that conducts the compressed air from the air-receiver to the place of work being soft and elastic, is comparatively little affected by the current of sand and air, unless the air is hot; hence methods to cool the air before it reaches the leading hose are necessary. Four such nozzles that gradually wear to ¾-inch diameter and then discharge 200 to 240 cubic feet of air per hour, require an air-compressor of 20 inches diameter for steam and 22-inch air-cylinders, by 24-inch stroke or approximate sizes, also a 150 H.P. boiler.

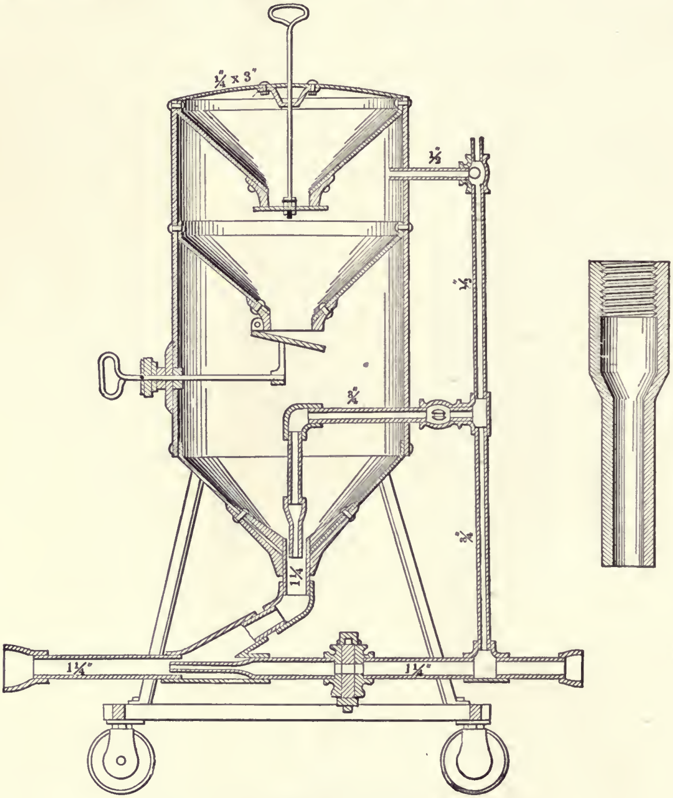

Fig. 40.—Portable sand-blast machine.

The abrading material, when used, must be thoroughly dry, and can be used four or five times over, or until it is broken into a powder too fine, or becomes too dirty to be effective.

For cleaning ships' bottoms in dry dock, where the rust and paint coatings are generally thick and somewhat softened by the water, about $\frac{8}{10}$ square foot of metal is cleaned per minute, or 48 to 60 square feet per hour. This costs about 3 cents per square foot of surface, as the waste of sand is greater and the work cannot be done so advantageously in a dry dock as in a shop.

On the New York Elevated Railway Station at 155th Street an average of 80 square feet per hour was maintained for a number of months in removing a hard coating of old paint and rust to the bright iron. The loss of time in changing nozzles and shifting scaffolds was about one hour per day per nozzle. The labor account was one man to hold and direct each nozzle; one man to attend to two sand-boxes, and one man to clean up and supply sand for the four nozzles or seven men per corps the men shifting their scaffolds without other aid. The four-nozzle plant for bridge or viaduct cleaning will clean about 2500 square feet of surface per eight-hour day at an expense of about $20 for all items, except the man and coal for the compressor, or 8 cents per square foot, which would be modified by the amount of cleaning for each structure.

Removal at the shop of mill-scale and dirt is done at the rate of 4½ to 5 square feet of surface per minute, or 270 to 300 square feet per hour per nozzle, or about ¼ cent per square foot of surface. With an organized corps and plant, the cost of cleaning surfaces need not exceed ⅛ cent per square foot of surface, large or small, or about one-third the labor-cost of the painter on a first-class coat of paint, and requires about the same degree of skilled labor as painting.

The metal-work of the movable dam at Lake Wennibioskish, Minn., erected during 1900, was cleaned bright by an extemporized sand-blast. A hoisting-engine run backward furnished the compressed air, an old steam-boiler was used for an air-receiver, gas-pipe for nozzles, and garden hose for leaders, etc.

Mr.W. C.Weeks, C.E.,* reports "that four laborers and one engineer in charge of the apparatus cost for labor $9.22 and $2.50 for fuel. On general surfaces, 40 square feet per hour were cleaned, using two nozzles,

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* *Engineering Record*, May 4, 1901.

or a cost of $0.036 per square foot. On plates and large straight surfaces, 90 square feet per hour was the usual rate of cleaning, which cost $0.016 per square foot."

In a number of United States navy-yards, with well-equipped, permanent, and fairly perfect sand-blast plants, the cost of cleaning averages ½ cent per square foot of surface. This for plates ½-inch thick is 98 cents; for ¼-inch plates, $1.95 to $2.00 per ton. To sand-blast 7-inch I-beams weighing 17.5 pounds per foot costs $1.35 per ton; 12-inch I-beams, weight 50 pounds per foot, cost 80 cents per ton.

The average cost for cleaning plate-girder bridges *in situ* is probably $1.00 per ton of metal. For truss and lattice-iron bridges the cost of sand-blasting ranges from $1.00 to $1.75 per ton.

The United States Army Engineer Corps cleaned 50,000 square feet of steel lock-gates and other metal on the Muscle Shoals Canal during 1898–99 from a temporary floating plant. The cost of all items, was 3 cents per square foot, and the new coat of paint cost 2.88 cents per square foot.

Mr. Geo. W. Lilly, C.E., reports the cleaning by sand-blast of a number of railway bridges and viaducts in the city of Columbus, Ohio. The work was done under exceptionally adverse circumstances, but indicated that 8 cents per square foot covered all the expenses. For cleaning a viaduct over the Little Miami Railway, containing 25,000 square feet of surface in a confined location where the cleaning was interrupted by the train-service that frequently amounted to one-fifth of the working hours, the cost of the work, including flagman, sand and drying, compressed air, and all other expenses, including the labor, was 3.04 cents per square foot. On the best days, in a favorable location uninterrupted by the trains, 1227 square feet were cleaned per day at a cost of 1.23 cents per square foot. On a plate girder containing 3727 square feet, the cost was 2.37 cents per square foot.

The pressure of air ranged from 25 to 38 pounds, averaging 33 pounds per square inch. The nozzles wore rapidly. They were of ½-inch extra heavy wrought-iron gas-pipe, about 2 feet long and lasted from 3 to 5 hours each.

The expense of handling structural metal at the shops after machining preparatory to sand-blasting it, ranges from 40 cents to $1.50 per ton according to the weight and character of the pieces and facilities of the plant.

A recognition of the fact that structural steel is a perishable material, requiring thorough protection from corrosion during all the stages of its manufacture and use, should be required of every engineer, and the subject should form an important part of his education. There is no part of structural engineering needing a more thorough reform in both spirit and practice than this one.

The apparent indifference regarding the future fate of steel material, after it is in location, is probably due to the mistaken economy of the engineer corps and the proprietors, on account of the added cost of properly cleaning the metal. If cleaning is necessary, as engineers and all admit, it should be specified in the contract, properly done, inspected by a competent person, and paid for like any of the other processes, and the penalty for its non-fulfilment be as strictly enforced as for a badly driven rivet or poorly machined or fitting part. The above deficiencies are readily detected and can be corrected, but the poorly cleaned surface escapes notice and is readily put out of evidence by the handy paint-pot.

It is the imperative duty of the engineer in charge of structural work to require his inspector to perform his duty at all times so that a radical change shall be had from the present practice of cleaning and painting ferric metal, the corrosion of which is now too much in evidence.

At a late meeting of an engineering society, the protection of ferric structures from corrosion was under consideration by oral discussion and correspondence. The cleaning of the surface of steel to the absolutely clean metal by some method, preliminary to the immediate painting of it under cover, was unqualifiedly endorsed. And yet within the limits of a ten-mile circle from the engineers' meeting there were many thousands of tons of ferric structural material in process of erection by the engineers represented at the meeting, and scarcely a ton of this material had received any other cleaning than that from a putty knife or a whisk-broom. The quality of the applied paint in many cases was as deficient as the cleaning. So much for theory *versus* practice.

Pickling the metal instead of sand-blasting it is more practised by European than American engineers, especially for structural work. Mill-scale is readily removed by immersing the metal in a hot dilute solution of sulphuric acid. Generally, 6 to 12 minutes suffices, using a 25 to 28 per cent acid solution. A 10 or 12 per cent solution is effective, but requires more time in the bath. The stronger solutions are recommended. They are equally as safe to handle and should be applied hot if possible; the latter quality is best for removing the scale.

In foreign navy-yards, 9 to 10 per cent hot solutions are used, the metal remaining in the bath five or more hours, according to the quality of the scale. This requires a large pickling plant and has no other advantages. When appearance or test shows the scale is loosened, the metal is removed and well washed by a copious and strong jet of water under 75 pounds or more pressure.

Soaking the metal in baths of still or light running water does not thoroughly remove the acid. The still-water bath is the cause of the failure of tin-plate.

Pickled metal is liable to become coated with a tough, gummy substance, quite difficult to remove, except by the friction from a strong jet of water. Arsenic in the sulphuric acid made from pyrites also adds to the gummy deposit precipitated on the metal. Acid free from arsenic should be specified for the pickle. The gummy deposit prevents the paint from bonding to the metal, rendering it liable to peel.

After the metal has been washed by the jet of hot or cold water it should be immersed in a bath of hot lime-water and be left in it long enough to reach the temperature of the bath, in order to neutralize any of the acid not removed by the water jet. It is then removed and dried, preferably in an oven. The coating of lime left upon the metal can be easily brushed off, leaving the metal clean and bright, which will show evidences of rust in an hour if not painted immediately.

Muriatic acid is sometimes used in place of sulphuric acid for the pickle. It is not as effective as sulphuric acid, it costs more, and the gummy coating formed by the pickle is more difficult to remove, requiring a hot alkaline or caustic-soda bath, instead of lime, to remove it. A solution of sulphate of zinc is effective for the removal of this gummy coating.

Obviously a pickling plant requires a larger space for an equal cleaning capacity than a sand-blast, and is not so convenient to use at all seasons of the year, and both are impractical to use in the construction tool shops.

The labor and material accounts for a pickling bath for all sizes and weights of ordinary structural steel is about 25 cents per ton. The labor account for moving the pieces into and out of the pickle, cleaning baths, and ovens, will be from 50 cents to $2.00 per ton, or rather more than is required for a sand-blast, as the several pieces, though of the same weight and character, have to be moved more frequently.

Steels high in carbon, or cast-iron articles, are difficult to pickle, as a film of graphitic carbon forms on the surface of the metal, which mixes with the gummy deposit from the acid bath, and requires considerable labor and care to remove.

When the sand-blast or pickling process is not available, mill-scale, rust, and old paint coatings are removed from works *in situ*, by the gasoline burning torch, followed closely by the scraper and wire brush.

The cost of the burning process is so closely connected with the painter's labor as to be difficult of separation, but a quart-burning torch will burn 3½ hours, and one man can saturate rust-spots and burn off from 80 to 100 square feet of surface per hour, at a cost of $\frac{6}{10}$ to $\frac{7}{10}$ cent per square foot of surface, leaving it ready for the painter.

A modern parlor, or sleeping-car, 65 to 70 feet long, requires three gallons of gasoline to burn off the *outside* paint coating, and about four days of time, for one man to use the torch, followed by two men two days each, to sandpaper ready for the painter, or a total cost of 45 cents for the gasoline, and $15.00 for the labor, or $\frac{8}{10}$ to 1 cent per square foot of surface.

Care is required in the use of gasoline, either for the torch, or for saturating the old paint, as explosions and serious burning of the workmen, and fires, are frequent. Insurance companies forbid the use of either the torch or fluid for the removal of paint or rust in any building covered by their policies.

Any material that can be inclosed in a chamber or iron casing and subjected to the action of a bath of low-pressure steam for 20 to 25 minutes will have the old coatings softened, when they can be easily scraped off. This is to be followed by a thorough washing with soap and water, and rinsing. A pair of locomotive driving-wheels required 30 minutes to scrape and wash after steaming. The total cost being about one-third to one-half that required for the usual caustic-soda application.

Many railway repair shops use the following mixture for the removal of old paint. It has no action upon rust. Caustic soda and sal-soda, each 30 pounds; mix with 3 pounds of strong ammonia diluted with 30 gallons of water. To the above, add a mixture of

30 pounds of finely ground quicklime in 5 gallons of water, and 3 to 4 pounds of melted laundry or soft soap. The two mixtures added together, when cold, should be of the consistency of putty. It is applied by a trowel or stiff 4-inch flat brush in successive coats about $\frac{1}{8}$ to $\frac{1}{4}$ inch thick. Care must be used in mixing the lime. A stirring-paddle should be left in the tub to form a vent to prevent the caustic mixture from blowing out.

The cost to remove the paint from a pair of locomotive driving-wheels by this mixture is 65 cents for material and 15 hours of labor at $2.25, or a total of $2.90. Careful washing with hot water to remove all traces of the caustic-soda paste is required, as for all strong alkaline mixtures.

Wooden surfaces treated with caustic-soda compounds to remove paint or varnish are injured by the raising of the grain of the wood, which cannot be restored by sand-papering. The parts so treated show spotted; even a staining-coat will not cover them uniformly. Fine woods are injured the worst.

CHAPTER XXIX.

FERRIC-PAINT TESTS.

Objection is made by some engineers and paint manufacturers to the immersion methods of testing paints; that they do not meet the actual conditions of coatings exposed to weather; that a ferric structure is not always wet, but wet and dry, with more dry hours than wet, etc. This would depend altogether upon the location of the structure; in many instances there might be more wet or damp hours than dry ones. A fog or long-continued sweat is more destructive to a paint coating than a passing storm. But the plain fact remains that these tests are all competitive as between different commercial paints, and under uniform conditions. The trial given one paint is given to all; the few successful ones are the better ones to select from to base any subsequent improvements or experiments upon, or for use. The water-test settles the merit of a protective coating in short order, and so soon as generally adopted by those ordering paints for the protection of ferric structures exposed to weather, so soon will the great majority of these patent paint compounds cease to vex the engineer with high claims and low performance.

The nearer any protective coating approximates an enamel or varnish, generally the more durable it will be. The Japanese and Chinese lacquers are varnishes, and dry better by the application of water than in dry air alone, and all compounded varnishes are hardened in the last stages of their drying by water. Lacquers when thoroughly dry remain unchanged for scores of years, when exposed to fresh or salt water either hot or cold or alternately wet and dry, or immersed for years. The coming ferric protective coating will probably be a true varnish with a carbon or graphite pigment. But it will be well to bear in mind that it will not be imperishable in exposed locations, and that its application and the preparation of the structure to receive it will require more attention than at the present time these matters receive; neither will it be a low-cost article.

Tests of Twenty-seven English Commercial Ferric Paints.

In a paper * read before the Newcastle, England, section of the Society of Chemical Industry, Mr. Henry Smith, F.I.C., described a series of experiments upon the protective powers of twenty-seven different English commercial paints, as applied to ironwork in fifty separate instances. The methods of test were those devised and employed by Mr. Max Toltz, C.E., in a series of experiments upon a number of American commercial protective coatings for iron in 1897.† Three sets of bright and clean iron plates, all of the same size, were respectively coated with the several paints, in all cases furnished as a stiff paste, and when applied, were brought to the consistency of a paint by mixing with genuine boiled linseed-oil, capable of drying in *seven hours under ordinary conditions of temperature, no driers* being used. The first coat was allowed to dry thoroughly firm before the second coating was applied. When this also was firm and hard, one set of the plates was exposed to the weather, as in ordinary cases of painted structures. The other two sets were treated as follows: One set was simply to corroborate the results obtained from the other set, the results being practically identical in each case. Each painted strip was placed in a clean, wide-mouthed glass bottle, half filled with clean pure water. The bottles were not closed, but were protected from the entrance of dust and impurities while allowing the air free access to the painted plates. Several of the plates had commenced to corrode in about a week. This was indicated by a cloudiness in the water, which afterward became further oxidized, and formed a red precipitate of ferric oxide, which subsided partly to the bottom of the vessel. After three months' exposure the plates were removed, and the liquid in each bottle, together with the sediment, was tested for the percentage of iron present in the form of rust.

The figure given as denoting the amount of corrosion is less than the actual amount, as it does not include the portion that adhered to the plate, and was not scraped or brushed off, and would not drain off. In each case the weight of rust was calculated to pounds of rust per 1500 square yards of painted surface; the other figures give the percentage composition of the several paints by weight.

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* *Engineer* (London) and the *American Gas Light Journal* (New York).

† September 4–20, 1899. *Journal of the Association of Engineering Societies*, St. Paul, Minn., 1897.

CONDITION AFTER THREE MONTHS' EXPOSURE.

Pounds of Rust from 1500 Square Yards of Surface.

			Corrosion.
6 samples of red lead alone, or mixed with barytes 50%;		raw oil, 10.00%	None.
Red lead. . .22.00%; barytes, 66.00%;	total, 88.00%;	“ “ 12.00%	“
“ “ . . .33.33%; “ 58.80%;	“ . .92.13%;	“ “ 7.87%	“
3 samples zinc oxide, “ 45.00%;	. . . .	“ “ 10.00%	Trace.
Zinc oxide. .27.27%; “ 63.63%;	“ . .90.90%;	boiled oil, 9.10%	“
White lead, pure 92.56%;	. . . .	“ “ 7.44%	75 lbs.
White lead. .53.78; barytes 40.33%;	“ . .94.11%;	“ “ 5.89%	80 “
“ “ 50.52%; “ 42.10%;	“ . .92.62%;	“ “ 7.38%	95 “
Iron oxide, pale (50% Fe_2O_3). .83.60%;	. . . .	“ “ 16.40%	81 “
“ “ deep (96% Fe_2O_3). .86.89%;	. . . .	raw oil, 13.11%	123 “
“ “ venetian red. . . . . . 7.55% Barytes. 80.57%	“ . .88.12%;	“ “ 11.88%	123 “
Iron oxide, medium color (94% Fe_2O_3). 86.89%;	. . . .	“ “ 13.11%	134 “
Iron oxide, extra bright color (90% Fe_2O_3). 82.35%;	. . . .	“ “ 17.65%	137 “
Iron oxide, pure (90% Fe_2O_3) . 76.30%;	. . . .	“ “ 23.70%	160 “
“ “ medium. . . . . .12.30% Barytes. 76.22%	“ . .88.52%;	“ “ 11.48%	244 “
Indian red (70% Fe_2O_3). 82.35%;	. . . .	“ “ 17.65%	227 “
Turkey red (95% Fe_2O_3). 81.16%;	. . . .	“ “ 18.84%	262 “
Iron oxide. . . . . .27.03% Barytes and calcium carbonate.62.52%	“ . .89.55%;	“ “ 10.55%	398 “
Barytes (natural barium sulphate). 88.00%;	. . . .	“ “ 12.00%	155 “
Iron oxide, venetian red. . . . . . 8.47% Barytes and calcium carbonate.78.80%	“ . .87.27%;	“ “ 12.73%	118 “
Iron oxide. . . . . .13.93% Barytes and calcium carbonate.60.00% Rose pink (principally barytes) .12.14%	“ . .86.07%;	“ “ 12.14%	242 “
Barytes and calcium carbonate.80.56% Celestial blue. 11.83%	“ . .92.39%;	“ “ 7.61%	266 “
Barytes and calcium carbonate.68.99% Ivory and carbon black. . . . . . . 8.42% Manganese dioxide. 2.46%	“ . .79.87%;	boiled oil, 20.13%	352 “
Barytes and calcium carbonate.79.30% Carbon and bone black. . . . . 4.35% Manganese dioxide. 1.30%	“ . .84.95%;	raw oil, 15.05%	392 “
Drop black (charcoal black). . .60.00%;	. . . .	boiled oil, 40.00%	250 “
Flake graphite, pure. 69.56%;	. . . .	raw oil, 30.44%	215 “
Boiled linseed oil, pure.			500 “
Raw Turkey umber. 51.85%;	. . . .	raw oil, 48.15%	510 “

Twenty mixtures of barytes alone, or with calcium carbonate mixed with celestial blue, Prussian blue, chrome-yellow, raw sienna, Vandyke brown, Italian ochre, Brunswick and other greens, chromate of lead, English umber, Turkey umber, ultramarine, Chinese blue, burnt sienna, mixed with raw oil in proportions from 11 per cent to 51 per cent of the weight of the paint; the corrosion in the order named above ran from 168 pounds to 441 pounds per 1500 square yards of surface.

Except in the case of the blues, umbers, siennas, etc., where the pigment had but little influence on the oil to resist decay beyond that inherent in the oil alone, the more separate substances that entered into the composition of the pigment, the more unreliable it became. A single exception is noted in the case of a Venetian red paint, made from barytes, calcium carbonate, and a small amount of iron oxide, that gave a better result than barytes alone, or when barytes was mixed with the other color pigments of much less specific gravity. Several substances in a composite paint are generally fatal to its protective qualities, no matter to what it is applied. The several atoms of these substances, even if uniformly distributed in the pigment in the process of grinding, bolting, and mixing (but they are not), will not retain their juxtaposition when mixed with the oil. The heavy atoms will sink, and there will be a marked difference in the coating spread from the top of the paint in the pot from that in the middle or bottom; the lightest and most perishable substances will get on the surface firs

Barytes worked well with red lead and zinc oxide, there being but a small difference in their specific gravities as compared with barytes and the other color cr base pigments. With white lead, as the percentage of barytes was increased, so was the corrosion. Aside from the reduction in cost of these lead and zinc pigments by the addition of barytes, there is no reason for its use, as the barytes alone did not give a satisfactory test. No doubt from the splintery character of its atoms, as has been before commented upon, it is wholly destitute of covering or coloring power. The vagaries of the iron-oxide paints in the varying proportions of the pigment and oil are noticeable, but not so marked as where barytes, one of the heaviest of all pigments, and calcium carbonate, one of the lightest, both classed as inert pigments, were mixed with the oxide, and fully sustained the previous remarks upon the non-protective character of composite and iron-oxide paints. Boiled oil, in the single instance reported, proved superior to raw oil as a vehicle for the several iron-oxide paints in the ratio of one to nearly five.

Smith's Dish-tests of Paints.

A second series of experiments were made by the same experimenter, and following the method of Mr. Max Toltz, C.E., to wit: A number of iron dishes five inches in diameter and one-half inch deep were scoured bright, and then coated with two coats of the several paints used upon the above-detailed iron plates and under the same conditions as to the composition and drying of the paints. These shallow dishes were filled with water and allowed to completely evaporate in the open air of the laboratory. This operation was repeated six times in the course of six months. Thus tested, the only paints which remained practically unaffected were red-lead and orange-lead paints, some of which, however, such as the "vermilionette" and scarlet-red paints, contained a'so a proportion of aniline colors, while two of the red-lead paints contained in the one case 45 per cent of barytes and in the other 66 per cent. All the other dishes were more or less rusted, the order of merit of the better paints being as follows:

1st. Zinc oxide.
2d. Equal parts zinc white and barytes.
3d. Zinc white, 3 parts; barytes, 7 parts.
4th. Lithopone (a mixture of zinc sulphate, zinc oxide, and barytes).
5th. Pure white lead.
6th. White lead, 5.37 parts; barytes, 4.03 parts.
7th. White lead, 5.05 parts; barytes, 4.21 parts.

All the other paints, thirty-six in number, proved inefficient. The first to show rust was that one painted simply with linseed-oil. The above classification of merit is by Mr. Smith, and, taken together with the detailed report of the glass-bottle test (before given), may be considered a fair representation of the protective qualities of the hundreds of commercial ferric paints foisted upon the market under various trade-mark names in the United States as well as in England, where the above experiments were conducted.

Both the immersion- and dish-tests are very important for determining in a relatively short time the weather-resisting power of a paint. If the coating is unable to resist the action of water or moisture in the form of steam, fog, or vapor from a tunnel or other confined space, it cannot be desirable for the protection of a ferric structure, or even a wooden one. The dish-test, probably, is the nearest to the actual condition which a paint must withstand. When the water in the dish is nearly evaporated, there remains in the circular seam of the bottom a film of water which contains the carbonic acid and the decomposing gases and dirt from the atmosphere, which act upon the paint in such a way that the coating at that part is soon permeated and rust forms. This action is more and more developed after each evaporation, and practically covers the whole dish in a short time. In actual service the same thing will happen. The corner of the dish finds its counterpart in every corner of a ferric structure where two plates, angles, or other parts join. Rust will commence at those seams and extend under the paint, but will not show as plainly on a bridge-truss as on the small dish.

Toltz's Tests of American Commercial Ferric Paints.

The shallow-dish tests by Mr. Max Toltz, C.E. (before referred to), were made prior and during 1897, and extended over a period of from six months to two years. Without entering into as great detail as that quoted from Professor Smith, the deductions from his tests are in brief. Twenty-two different paints were submitted to test under the following classification:

No. 1. True asphaltic varnish paints compounded by heat in the same manner as a black baked japan, and practically of the same nature and comparable therewith. No corrosion reported after the dishes had been filled and evaporated naturally fourteen times.

No. 2. So-called asphaltic varnishes, or paints of inferior qualities to the above No. 1, made from asphaltum dissolved in benzine or other volatile vehicle, *but were not a true varnish.* They contained about 43.5 per cent of vehicle and 56.5 per cent reported to be asphaltum. As a rule they showed well in the beginning, but after the volatiles had evaporated, especially when subjected to a moderate heat-test, the coatings became quite brittle, were easily removed by abrasion, and did not protect the surface covered with them. Their composition varied in the several specimens tested. One sample analyzed had *no asphaltum* in it. Under test the dishes painted one coat showed considerable rust all over after the fifth exposure. Those painted two coats after the seventh exposure showed not much better. Generally, their reliability as protective coverings for ferric structures is the least satisfactory of all paints.

No. 3. Black-carbon paints, in which the vehicle was practically a varnish, the carbon-black and other pigments being ground in practically a linseed-oil varnish, and are comparable with No. 1, to which they are closely related. The dish painted with only one coat showed a little deterioration at the end of the fourteenth evaporation, while the dishes painted two coats were uninjured, the coating being as elastic and tough as when first applied.

No. 4. Iron-oxide paints consisting of more or less iron oxide with more or less silicious matter, and compounds of lime and magnesia. They were of different grades and qualities, were as a rule well ground and spread well. Under test on the dishes painted with one coat, after the fifth exposure many rust-spots appeared. Those painted two coats were refilled six times, and on them the rust was plainly discernible to the eye.

No. 5. Graphite paints and silica-graphite compounds. These paints were received from the several manufacturers in the form of a stiff paste, and when mixed, ready to apply, 4½ parts of paste to 3½ parts, by weight, of boiled linseed-oil were used. The dishes painted with one coat were evaporated ten times. After the fifth evaporation a few specks of rust were noticeable, and the number gradually increased after each successive evaporation. After the tenth exposure some slight difference between them was noticeable, but not much. The dishes painted *two coats* were exposed thirteen times in two years, and none of them showed any rust or indication of rust. The natural toughness and elasticity of the paint still remained.

It will be noted that there is a wide discrepancy in the results of the dish-test of Mr. Toltz, as above, of the graphite paints, both the natural amorphous pigments and the compounded silica-graphite pigments, and the plate-test given by Professor Smith of *pure flake-graphite* mixed with *raw linseed-oil* that gave 215 pounds of corrosion to 1500 square yards. This, no doubt, is due to the repellent nature of the pure flake-graphite; the pigment does not take kindly to the oil, any more than soapstone does. Raw oil, even if pure, contains from 5 to 7 per cent of water, that renders a combination of the graphite and oil quite uncertain unless under the influence of heat. The boiled-oil vehicle with pure flake-graphite, used by Professor Spennrath in his experiments (hereafter referred to) with paint-skins detached from the metal surfaces, withstood an exposure in a pure water-bath for six weeks without injury other than a slight loss in weight of the skin. Moisture in the oil in this case was eliminated, as in the case of Mr. Toltz's graphite paints, and the merits of boiled oil as a vehicle for most paints over raw oil is sustained in these experiments, as it is in daily practice elsewhere.

United States Navy-yard Paint Tests.

The result of these tests corroborate the series of tests made by order of the Secretary of the United States Navy in 1884–5.* By request, sixty paint firms submitted seventy-five different paints for test, which were applied to five hundred test-plates, and then immersed in sea-water at four navy-yards, and upon one government vessel in service. The paints that successfully withstood the test and received an *order of merit,* were red lead, zinc oxide, carbon, and graphite compounds. The so-called asphaltum paints were at the bottom of the list in the *no-merit column.* Evidently there has been slight improvement, if any, in this class of paints since the date of the U. S. Navy tests to the present time, and one can but wonder, in the face of repeated and recorded failures, that they ever receive an application to a ferric structure, ashore or afloat. Lead, zinc, carbon, and graphite compounds maintain their supremacy for government work. In other tests of commercial and special paints, where the tests have been carried to the destruction of the coating as a whole, the partial destruction of the vehicle was generally followed by the disintegration of the weaker substances comprising the pigment, such as the carbonate and sulphate of lime, asphaltum, iron oxide, and the various color pigments, viz., the ochres, umbers, blues, greens, carmines, yellows, etc. The only pigments practically unaffected by the destructive element were the graphites, the silica, barytes, slag, slate, and brickdust. Other adulterants were but little affected, some of them being partly recoverable, which was also the case with the red lead, white lead, and zinc-oxide pigments.

Commercial Coal-tar Paints.

Fourteen commercial paints, principally of the coal-tar and asphalt class, were tested under uniform conditions, viz: Wrought-iron plates, free from mill-scale, were coated with two coats each of the following paints. All of the coatings were perfectly dry before the second coat was applied. When the second coats were dry and

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* Transactions American Society Mechanical Engineers, 1894, Vol. XVI, Paper No. 625, pp. 399–402.

hard, one set of the plates was immersed for two months in sea-water, and another set was exposed to atmospheric influences, where combustion gases from locomotives and coke ovens reached them freely at all times, this exposure being similar in all respects to that of railway-bridge paints.*

No. 1. *Carbonizing coating* (Cohen Mfg. Co.).

Physical properties.—Very black, good body, spread well, and covered a large surface, coating smooth.

Drying properties.—Poor.

After 24 hours, wet.
“ 48 “ quite wet.
“ 72 “ slightly wet.
“ 96 “ dry.

Physical test.—In sea-water, much rusted and blistered, paint easily rubbed off, and in bad condition. Atmospheric exposure, condition of coating, fair.

No. 2. *Durable metal coating* (Edward Smith & Co.).

Physical properties.—Brownish color, thin and required a large quantity to cover; adhered poorly; coating thin and uneven.

Composition.—Linseed-oil, asphaltum, and kauri-gum

Drying qualities.—Dried slowly.

After 24 hours, wet.
“ 48 “ tachy.
“ 72 “ slightly tachy.
“ 96 “ dry.
Second coat dry in 7 days.

Physical tests.—In sea-water, much rusted, peeled off easily, and blistered.

Atmospheric exposure.—Rusted badly on edges of the plate.

No. 3. *Turpentine asphaltum* (C. A. Reeves & Co.).

Physical properties.—Coating thick and uneven; required a large amount to cover. Spread poorly; adhered well.

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* Transactions American Society Mechanical Engineers. Experiments by J. H. Pennock, Chemist. Vol. XXII, 1900, 1901, Paper No. 901.

Drying properties.—

After 24 hours, quite wet.
" 48 " tachy.
" 72 " almost dry.
" 84 " dry.

Physical test.—In sea-water, much rusted, paint peeled off in spots; did not rub off as easily as No. 2. In two spots corrosion had *eaten through* the plate.

Atmospheric exposure.—Condition very bad, rusted all over.

No. 4. *"B." Black varnish* (Mica Roofing Co.).

Composition.—A coal-tar product, contained light oils, naphthalene and anthracene, not indicating much pitch.

Physical properties.—Very fluid, gave a smooth coating.

Drying properties.—

After 24 hours, wet.
" 48 " quite wet.
" 72 " slightly wet.
" 96 " dry.

Physical test.—In sea-water, fairly free from rust, but coating was rough and uneven, broken off in many places.

Atmospheric exposure.—Rusted badly along the edges.

No. 5. *Asphaltum paint* (C. E. Mills & Co.).

Composition.—Asphaltum, petroleum, and some linseed-oil.

Physical properties.—Thickens on exposure to air; gives a thick uneven coat.

Drying properties.—Dry in 56 hours.

Physical test.—In sea-water, much rusted and blistered, large part of the plate coating entirely gone.

Atmospheric exposure.—Plate in very bad condition.

No. 6. *Black diamond paint* (C. W. Reeves & Co.).

Composition.—Pitch and dead oil.

Physical properties.—Quite fluid, spread well and adhered well and gave a good even coating; smells of coal-tar.

Drying properties.—

After 24 hours, slightly tachy.
" 36 " almost dry.
" 48 " " "
" 60 " dry.

Physical test.—In sea-water, did not blister, rusted considerably, paint off in spots. Not so good condition as No. 4, but better than Nos. 1, 2, 3, and 5.

No. 7. *"A." Varnish* (Mica Roofing Co.).

Composition.—Asphaltum, in petroleum spirits.

Physical properties.—Fluid, spreads well and adheres well; gave a thick coating fairly smooth, smells strongly of petroleum spirits.

Drying properties.—

After 24 hours, quite wet.
" 48 " slightly tachy.
" 60 " dry.

Physical test.—In sea-water, much rusted, not blistered, paint off in numerous spots. In bad condition.

Atmospheric exposure.—Badly rusted.

No. 8. *Mineral rubber* (Assyrian Asphalt Co.).

Physical properties.—This paint was so thick and viscous that it could not be applied without thinning. When thinned with naphtha it did not work satisfactorily, and the experiments with it were abandoned. (See Chapter XII.)

No. 9. *Black roofing paint* (Samuel Cabot).

Composition.—Pitch dissolved in light petroleum oil.

Physical properties.—Fluid, gave a smooth coating that adhered well. Smelt of tar-oil.

Drying properties.—Dried in 56 hours.

Physical tests.—In sea-water, rusted badly, coating off in many spots, rubbed off easily.

Atmospheric exposure.—Rusted badly all over.

No. 10. *Black paint* (Thomas Mfg. Co.).

Composition.—A coal-tar paint with a heavy oil menstruum.

Physical properties.—Much like No. 9.

Drying properties.—

After 24 hours, wet.
" 48 " tachy.
" 60 " dry.

Physical tests.—In sea-water, paint came off easily; many rust-spots.

Atmospheric exposure.—Condition fairly good.

No. 11. *Slag cement paint* (Barrett Mfg. Co.).

Physical properties.—A coal-tar paint, producing a coating similar to Nos. 9 and 10.

Drying properties.—Dry in 60 hours.

Physical tests.—In sea-water, had a tendency to peel off; some rust-spots noticed.

Atmospheric exposure.—Plate badly rusted.

No. 12. "*Ferrodor*" (Wm. Somerville's Sons).

Composition.—Graphite, turpentine, oxide of iron, and linseed-oil. A compound or patent paint.

Physical properties.—Color, purplish gray; coating, very thin; three coats recommended by the manufacturers.

Drying properties.—Dry after 48 hours.

Physical tests.—In sea-water, paint peeled off badly, plates very much corroded, bad condition generally. The graphite settled to the bottom of the can in a tenacious pasty mass, and the paint was spread with great difficulty.

No. 13. "*Antoxide.*" Ready mixed paint (Harrison Bros.).

Physical properties.—Bright-red color due to red lead; very fluid; spread well, giving a smooth even coating that adhered well.

Drying properties.—Dry after 48 hours.

Physical properties.—In sea-water corroded badly, paint peeled off, plate much rusted.

Atmospheric exposure.—Paint turned black, plate badly rusted and scaled off.

No. 14. "*Crysolite*" (Solvay Process Co.).

Composition.—A paint made from coal-tar (special process).

Physical properties.—Deep-black color; spread well and adhered well, giving a smooth even coating, rather thick; contained 10 per cent free carbon.

Drying properties.—Dry in 36 hours.

Physical tests.—In sea-water no corrosion or blistering; had a slight tendency to peel.

Atmospheric exposure.—Plate slightly rusted; stood the action of combustion gases better than any of the other competitive paints. There was no tendency of the paint to run or crawl when applied to any metallic surface at ordinary temperature. (See Water-pipe Coatings, Chapter XII.)

A number of commercial ferric paints were tested (1899) by Prof. Ira O. Baker for their comparative resistance to heat, sea-water, strain, elasticity, the fumes of sulphuric and nitric acids also carbonic acid, with the following results:*

The samples of paint named were furnished by the manufacturers *for the purpose* and mixed with linseed-oil as directed by them, and spread on clean bright wrought-iron test-plates.

Reference Number.	Kind of Paint.	Weight per Gallon.	How Received from the Maker.
		Pounds.	
1	Red lead.	31.72	Dry pigment.
2	White lead.	21.24	Paste.
3	Purple iron oxide.	11.34	Mixed ready for use.
4	Chattanooga iron oxide.	14.13	Dry pigment.
5	Williamsport iron oxide.	12.99	Mixed ready for use.
6	Detroit superior graphite. . . .	9.49	" " " "
7	Mexican graphite.	8.57	Dry pigment.
8	Dixon's graphite.	8.84	Mixed ready for use.
9	Trinidad asphalt.	9.52	" " " "
10	Bessemer paint.	13.09	" " " "
11	Carbonizing coating.	9.61	" " " "
12	Lithogen silicate.	17.06	Paste.

A sample of each paint in one and two-coat work was exposed to heat and the products of combustion in the smoke-flue from a boiler burning bitumnous coal. The condition of the plates on removal was:

1. Red lead.—Entirely dead and very brittle. The powdery residue was easily removed, bringing into view the base metal.

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* *Railroad Gazette* (New York), March 10, 1899.

2. White lead.—Blistered and baked. Coating was brittle and entirely dead, and very easily removed. Removal of the residue exposed the base metal.

3. Purple iron oxide.—Covered with blisters. Paint soft and easily removed. Removal of the blisters exposed the base metal only to a slight extent.

4. Chattanooga iron oxide.—Considerably blistered, moderately soft, adhering well. Removing the blisters did not expose the base metal.

5. Williamsport iron oxide.—Covered with blisters. Paint tenacious, adhering well. Removing the blisters exposed the base metal.

6. Superior graphite.—Small blisters. Paint hard and difficult to remove. Almost impossible to expose the base metal.

7. Mexican graphite.—Soft and readily removed. Removal of blisters did not expose the base metal.

8. Dixon's graphite.—Very few blisters. Paint hard and very adherent.

9. Trinidad asphalt.—Smooth; considerable of the paint melted and ran off. The portion remaining was hard and brittle.

10. Bessemer paint.—Soft and hard to scratch off.

11. Carbonizing coating.—Ridges very conspicuous. Paint firm and adherent. Removal of blisters exhibited a very porous, loose structure of the paint.

12. Lithogen silicate (white paint).—Substantially the same as the white lead.

Effect of salt water.—A set of the plates were exposed to a saturated solution of sea-salt (brine) for seven weeks, the plates being frequently withdrawn and allowed to dry. Their condition at the end of the exposure was:

1. Red lead.—Hard and adhering. Metal clean and bright under the two coats, but badly rusted under the single coat.

2. White lead.—Hard and adhering. Clean metal under two coats, rust under the single coat.

3. Purple iron oxide.—Firm and adhering. Occasional rust-spots throughout.

4. Chattanooga iron oxide.—Firm and adherent. No rust anywhere.

5. Williamsport iron oxide.—Firm, and adhered only fairly well. Metal under two coats bright, but under the single coat considerable rust.

6. Detroit superior graphite.—Hard and adhering well. Rust under the single coat, none under two coats.

7. Mexican graphite.—Elastic and easily removed. No rust.

8. Dixon's graphite.—Good condition. Elasticity only slightly impaired. Easily removed no rust.

9. Trinidad asphalt.—Seemingly unaffected. No rust anywhere.

10. Bessemer paint.—Moderately hard, peeled off easily, no rust.

11. Carbonizing coating.—Peeled off easily. Rust beneath both the one and two coats.

12. Lithogen silicate.—Hard and adherent. No rust-spots.

No report was made of the condition of the paints exposed to atmospheric influences, evidently for the reason that the exposure period had not been long enough to materially affect any of the paints when the test closed.

A set of the plates were exposed to the fumes of strong sulphuric-, nitric-, and carbonic-acid gases for five weeks. The action of the sulphurous gas was characterized by its bleaching power upon the paints and the disintegrating effect on the iron under the paint, also the formation over the entire area of blisters, under which was found a moderately hard whitish deposit.

The order of merit for the several paints was: Trinidad asphaltum, Carbonizing coating, Dixon's graphite, Red lead, Lithogen silicate, Mexican graphite, Purple iron oxide, Superior graphite, Bessemer paint, Chattanooga iron oxide, Williamsport iron oxide, White lead.

The effect of the nitric-acid gas was substantially the same as the sulphurous gas, except that the single coatings of the paints were completely destroyed. The order of merit for the double coatings was: Trinidad asphaltum, Lithogen silicate, Red lead, White lead, Purple iron oxide, Superior graphite, Mexican graphite, Chattanooga iron oxide, Williamsport iron oxide, Dixon graphite, Carbonizing coating, Bessemer paint.

The carbonic-acid gas in large quantities, supplemented by moisture, had only an almost imperceptible effect upon any of the paints.

To test whether any of the paints would crack during the elongation of a painted bar, strips of machine steel $2'' \times \frac{1}{2}'' \times 18''$ were painted two coats, and after drying for two months were submitted to a strain of 16,000 pounds per square inch; the paint in every case remained firm and close-adhering. The stresses were then increased slowly beyond the elastic limit of the steel, and in no case did the paint crack before that point was reached.

It was noticed that after passing the elastic limit of the steel, the paints were marked by a series of lines arranged in herring-bone patterns, that were alike on both sides of the bar and alike situated. Evidently the lines were due to a rearrangement of the atoms of the steel bars while under strain, the centre atoms moving less freely than those near the corners and edges of the bars, the paint naturally following the particles of steel that they covered. Naturally the heavier coatings of the paints were the least elastic. The order of merit in the elasticity test was: Trinidad asphaltum, Carbonizing coating, Purple iron oxide, Dixon graphite, Mexican graphite, Superior graphite, Williamsport iron oxide, Chattanooga iron oxide, Bessemer paint, White lead, Red lead, Lithogen silicate.

CHAPTER XXX.

PAINT TESTS ON RAILWAYS.

New York Elevated Railways.

THE physical condition and the extent of corrosion on all parts of these structures have been freely commented upon by the technical engineering journals and the daily press. When originally erected, no attempt was made to remove the mill-scale, and none has been made since, presumably because of the impossibility of its success, and the cost. The composition of the paint which has been repeatedly applied to them has been kept very uniformly good in quality, but its application has been solely for appearance, as no paint can now reach the seat of corrosion underlying all the coats of scale, dust, cinders, and paint.

The renewal of the whole structure will probably be necessary in less than a hundred years from its erection.

The composition of the paint used is given by the chief engineer as follows:

FOR FIFTY GALLONS OF PAINT, OLIVE-DRAB COLOR.

	Summer Formula.	Winter Formula.
White lead, Jewett's best	300 pounds	275 pounds
Bridgeport zinc oxide, strictly best quality	175 "	150 "
French ochre " " "	100 "	90 "
Prussian blue " " "	1 "	1 "
Lampblack " " "	½ "	½ "
	576½ pounds	516½ pounds

The above pigments are ground in Campbell & Thayer's raw linseed-oil. The weights given include the necessary oil to grind the pigments to a paste.

When applied, it was mixed with

	Summer Formula.	Winter Formula.
Boiled linseed-oil, Campbell & Thayer's	8 gall.	9 gall.
Raw linseed-oil, " " "	15 "	15 "
Spirits of turpentine, first quality	3 "	3 "
Liquid or japan drier, " "	2 "	3 "
	28 gall.	30 gall.

New York Elevated Railway Viaduct.

The viaduct over the Harlem Station of the New York Elevated Railway at 155th Street was oil-coated, and received iron-oxide paint coatings at the time of its erection, and within five years of its completion had developed corrosion to such an extent that in 1897 the sand-blast was used to clean it preparatory for another effort for its preservation. This sand-blast process cost about $10,000, or over fifteen cents per square foot to apply, or about seven times more than a properly selected method of procedure and paint would have cost in the first place, and then only the lower and accessible sides or parts in sight received treatment. About 50,000 square feet of surface was cleaned by the sand-blast, to the bright iron, removing about 12 tons of old paint, scales of rust, and cinders, showing a unmber of distinct layers of highly corroded matter.

Seventeen panels of lattice-truss, floor-beam and buckle-plates, supporting the paved carriage roadway and footpaths overhead, about 2825 square feet of surface each, and numbered consecutively 1 to 17, were then painted with the same number of selected protective coatings furnished by a like number of paint firms in competition with each other. The several coatings were applied in strict conformity to the directions received with each brand of paint, the application being to the bright iron as left by the action of the sand-blast, and within 3 to 4 hours from the time the sand-blast ceased action. Every possible condition was brought into bearing to make the test one of a practical and commercial nature as well as of scientific value, absolutely without prejudice or favor in any respect. From the prominence of the structure in an engineering view, and its situation exposed to storms, sea air, fog, cinders, steam, and gases from scores of locomotives in constant service beneath it, nearly all of the metal being within a few feet of the tops of engine-stacks and receiving the products of combustion under blast-action and in an approximately closed space, the future result was anxiously looked for as an important demonstration of the practical value of the several best protective coatings in the market.

After an exposure of about nine months, and while a few of the coatings, viewed from the station platform, showed slight evidences of failure, a thorough examination of the condition of each panel was made by a prominent civil engineer of New York City. This report is of extreme interest, and is summarized, viz., 100 rating as a perfect condition of the coating.*

Number of Panel.	Number of Coats of Paint.	Kind or Name of Paint.	Rate of Drying.	Freedom from Rust, Per Cent.	Reference Marks as to Condition.
1	3	Lead, graphite and lucol-oil.	Medium	97	*a*
2	2	Amorphous graphite, Detroit Co.—L.S.G.	Slow	80	*b*
3	2	Red lead, antoxide, F. and D.	Fast	25	*c*
4	2	Graphite (kind not stated).	Slow	75	*d*
5	3	Nobrac (trade mark).	Medium	99	*e*
6	2	Carbon Black (F. W. Devoe & Co.).	Slow	85	*d*
7	2	Durable Metal Coating (E.Smith's varnish)	Slow	75	*d*
8	2	Black Manganese (iron paint)	Fast	30	*f*
9	2	Carbonizing Coating (trade mark).	Slow	80	*a*
10	4	Mineral Rubber (no particulars).	Fast	78	*g*
11	2	Black varnish (composition not given). . .	Medium	58	*h*
12	2	Carbon paint (no particulars).	Medium	92	*a*
13	2	Graphite (Standard Oil Co.). Kind not stated.	Medium	67	*a*
14	2	Dixon Co. Silica graphite, mixed paint. . .	Slow	70	*d*
15	2	Asphaltum (California Co. brand).	Very Slow	65	*j*
16	2	Ruberine (trade mark). Coal-tar composition.	Medium	58	*k*
17	2	Black diamond (trade mark).	Medium	70	*l*

a. Very little rust. Paint crumbles in places as though rotten. Easily removed.

b. Fair condition, but discolored; rust coming through.

c. Very badly rusted.

d. Rusty, but not deep.

e. Slight rust on top flange of one girder; rest of girder clean.

f. Rust very deep; buckle plates bad.

g. Area of rust-spots small; rust not very deep.

h. Rust very bad and deep.

j. Deeply rusted; buckle plates still good.

k. Rust very deep and angry; buckle plates mildewed.

l. Small pimples of rust, as though formed under the paint.

Panel No. 1 was an *outside one*, and the first to be sand-blasted and painted, in some parts with two and in others three coats of paint, in the clear hot days of summer, a material advantage in its favor. The sand-blast was then shifted to the southern end of the viaduct; and panel No. 17, also an *outside one*, was the next one cleaned and painted in hot clear weather, and so on consecutively, in

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* *Engineering News*, September 23, 1897, Illustrated; *Engineering Record*, September 25, 1897, Illustrated.

the reverse order of the panel numbers, back to No. 1; panels Nos. 7 to 2 having been done late in the fall under unfavorable conditions as to the spreading and drying of the paint in addition to the other objectionable conditions. About 80 square feet of panel surface was cleaned per hour, or 600 square feet per working day; each panel requiring from five to six days to clean and paint it.

At the end of about a year the condition of all of the paints was so unsatisfactory that the viaduct was repainted without removing, only in a perfunctory manner, the old test coatings with their fast-forming burdens of rust; and this competitive test came to an inglorious end.

The result could have been foreseen from the first, before a single truss or pound of material had been placed in position, or was even out of the construction shops, had not commercial greed, official indifference or ignorance, either one or all, ruled the matter.

The destruction of the tubular railway bridge over the St. Lawrence River at Montreal, Canada, had not become a fact so musty with age as to have escaped attention concerning the dangerous effect of hot combustion gases upon any paint coating in a confined space. Corrosion history blindly repeated itself when the viaduct material was first painted by the contractors, then repeated the "Comedy of Errors" when it was erected and again when it was sand-blasted for its final fiasco. The plain facts of the painting after the sand blast action are, that the coatings were destined for an early destruction from the beginning, by reason that the first coat was applied in an atmosphere saturated with the hot vapors of combustion and steam, which were so corrosive that the freshly cleaned surface of the metal showed a blush of rust within an hour after cleaning, and if left for three hours the rust could be wiped off by the hand. The paints were spread in this atmosphere, and before they could in any measure dry, so as to be in any degree resisting, they were thoroughly impregnated by the hot gases and steam which left their condensed strength upon the surfaces of the green paints. The second and subsequent coats were not only applied under the same atmospheric conditions as to the hot vapors and cinders, but had the condensed products of combustion sandwiched between them. Probably a baked japan or Bower-Barff coating are the only ones which would have successfully met the situation, which is an exceptional one. Such coatings applied at first, would not have cost one-half as much as the sand-blast and the several coatings applied in the first and subsequent stages, and would have been thoroughly protective and avoided nearly all the future expense in the care of the structure so far as the painted surfaces are concerned.

A paint test of an extended character has been in progress for the past few years by Mr. Geo. W. Webster, C.E.,* to determine the best paints for use on the city street iron bridges, crossing the railroads within the city limits of Philadelphia, Pa.

Fifty-four sample plates of iron 12″×24″ were coated by twenty-two manufactures of paint, and exposed at a number of places on the street viaducts, in situations that were as nearly uniform for the several competitive coatings as possible to provide. The test coatings were changed in their location as circumstances required to equalize the exposures, which were very severe, the clearance between the top of the locomotive stacks and the metal work of the bridges being only two to three feet.

The samples of paint submitted included the most prominent proprietary paints, including the carbon and graphite classes.

The results of only a few months' test demonstrated that on the lower surfaces of the plates on the bridge structure no paint was able to resist the mechanical injury from the sand-blast action of the locomotive exhaust. These situations are now protected from this action by wooden sheeting a few feet in width on the line of the exhaust.

On the upper side of the test-plates, subject to moisture, combustion gases, and deposits of cinder, the results were more satisfactory, but were not conclusive as to the relative merits of the samples, due to the difficulty in comparison on the basis of truly identical conditions.

The general trend of the results was, the subsequent selection of certain of the proprietary paints for a trial on bridges, and component parts of bridges, under a general formula, having red lead as the principal pigment, viz:

Red lead, two coats over shop coat of raw linseed-oil for inclosed space of structures.

Red lead over shop coat of raw linseed-oil and two coats of white lead three parts, and zinc oxide one part, for the field work.

Indian red, one coat over shop coat of oil. Red lead, third coat.

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* Chief Engineer's Bureau of Surveys, Department of Public Works, City of Philadelphia, Pa., 1902.

Indian red, one coat over shop coat of oil. White lead three parts, zinc oxide one part, for field work.

The Gray's Ferry deck bridge over the Schuylkill River was included in the test, being painted with the following paints, all applied as a first or shop coat:

Nobrac, lucol-oil paint, rubber paint, Bessemer paint, antoxide, durable metal coating, red lead. Above the deck for the second full coat, red lead was applied, except in one case, where white lead and zinc oxide were used. Below deck, for the third full coat, the same paint was used as for the shop coat, except in one case where white lead and zinc oxide were used for both the second and third coats.

The above coatings were applied in 1899-1900, and the time since then has been too short to note any material difference in their condition. The general practice in painting ferric structures by the Board of Public Works of the city of Philadelphia for a number of years has been the use of red lead and lampblack for a first or priming coat at the shop, followed by two coats of the same paint in different shades of chocolate color for the field coats, though in some cases white lead and zinc oxide have been the field coats. That the above paints have *not proven* satisfactory in the presence of combustion gases and other influences incident to their location is evident from the above experiments to correct their deficiencies. In connection with the same matter, it may be of interest to note that the train-shed roof of the Broad Street Station of the Pennsylvania Railroad at Philadelphia, which was painted with red lead and lampblack, is seriously affected by the corrosion of the roof-trusses. This structure has had extremely good care since its erection; but corrosion has established itself, owing to the early decay of the red-lead coatings, and will soon require cleaning by the sand-blast to correct the mistake of using red lead for train-shed painting. (See Chapter XXXVI, Changes in Pigments.)

Influences that Affect Paints.

Some of the influences that affect the life of a paint coating have been determined by the experiments of Prof. J. Spennrath,* from whose essay the following excerpts are selected. The experiments were made upon paint-skins alone, not upon a painted surface. The skins were made from chemically pure, finely ground flake graphite

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* "Protective Coverings for Iron." *Railroad Journal,* New York, 1896.

and linseed oil, applied to zinc plates in two coats, each of which was allowed to harden thoroughly. The plates were then placed in a dilute solution of sulphuric acid and the zinc dissolved. The paint-skins were then used for testing by immersion and exposure for six months in a number of liquids and gases, as follows:

Immersion Tests.

In pure rain-water the skin remained cohesive, even elastic, was of dull color, noticeably injured, and lost in weight	10.4	per cent.
In sea water the skin remained uninjured in texture and lustre, with a small loss in elasticity, and in weight	4.52	" "
In a 10 per cent solution of common salt the skin was but little affected in lustre and elasticity, but lost in weight	2.4	" "
In a 10 per cent solution of sal-ammoniac the skin was unchanged. Lost in weight	3.5	" "
In a 5 per cent solution of sulphuric acid the skin remained unchanged. Lost in weight	1.65	" "
In a twenty-four-hour immersion in hot water 160° to 170° F. the skin was materially affected in texture and color. Lost in weight	9.83	" "
In an aqueous solution (alkaline) of mineral-coal ashes the skin was materially affected. Lost in weight	14.8	" "
In a 1 per cent solution of soda the skin after three days was vividly affected, and after a few days, more exposure was destroyed.		
In a 5 per cent solution of nitric acid the skin was destroyed.		
In a 10 per cent solution of the chloride of magnesium the skin was unchanged, but lost in weight	1.1	" "

Exposure Tests in Closed Vessels.

Over sea-water for six months the skin was uninjured in color or texture, but had become somewhat viscous; no loss in weight.		
Over dry chloride of calcium (anhydrous) the skin was not at all affected, and gained in weight	0.46	" "

Over acetic acid, fuming muriatic acid, nitric acid, ammoniacal liquor, liquid sulphate of ammonium, a solution of gaseous sulphurous acid and water, all the skins were destroyed in a few days.

A skin made from red lead and linseed oil, exposed for forty-eight hours to an atmosphere of hydric sulphide, became black and rough, dull in lustre, and increased in weight.............................. 1.5 per cent.

The changes here indicated relate solely to the vehicle, as the graphite pigment was passive to the action of any of the destructive agents. Wherever the skins were destroyed every other oil-paint coating would have been likewise destroyed, whatever pigment was in it. In the other cases where changes in the vehicle are noted, the change of the skin appears to be wholly unlike that which would have occurred had it been attached to any surface. The professor has evidently found this to be the case, judging from some of his notes preceding the record of his tests. There are commercial paints—notably those made from amorphous mineral graphite, that containing less graphitic carbon, and combined with silica and a small amount of mineral oxides—that would have afforded a better protection to the vehicle than the chemically prepared graphite used in these experiments, the cost of which would probably bar it from forming any part of a protective covering for iron.

Spennrath's Temperature Tests.

A number of graphite paint-skins of the same character as those used in the above immersion and exposure tests; also, some three-coated skins made with other pigments and linseed oil and mixed with turpentine and other driers, and mineral oil, were submitted to constant temperatures of 122°, 203°, and 248° F. for five days. Briefly the results were:

All the skins shortened from 1.2 to 4.3 per cent, averaging 3.76 per cent, and lost in weight from 2.11 to 8.3 per cent, averaging 5.82 per cent; the greatest change occurring in the single instance of a graphite skin exposed for five days to a temperature of 248° F., which shortened 5 per cent and lost in weight 9 per cent.

The smallest change was also in a graphite skin exposed for five days to a temperature of 120° F., that shortened 1.2 per cent and lost in weight 4.4 per cent, and, though visibly affected in elasticity, was changed the least in other respects. All the other skins became brittle and stiff, broke easily when bent sharply, and were darkened in color. The white-lead skin changed to a faint yellow, the sulphide of lead and zinc oxide skin to an intense yellow.

The addition to the linseed oil of 10 per cent of either the oil of turpentine or other driers, or a mineral oil, or other fatty non-drying oils, including some gum copal, had no effect whatever to resist the changes effected by the heat. Not more than 10 per cent of mineral oil could be added to the linseed oil, as it rendered the paint viscous after drying. The Bessemer paint-skin, the pigment being a ground furnace slag, and the linseed-oil vehicle having an addition of a non-drying fatty oil with some gum copal, was just as sensitive to the heat as any oil paint.

Generally the action of the heat was less marked upon the graphite skins, which were less brittle than those made from white lead or zinc-white. The red-lead skins were especially sensitive to mechanical influences.

These changes are easily accounted for. The oily, repellent nature of the flake graphite prevented it from bonding to the oil vehicle as firmly as the other natural pigments and those of higher specific gravity will do in both a green or a thoroughly dried paint. While it is generally known that heat is destructive to oil-paint coatings, it does not follow that the coatings are so sensitive to its action that it may be deemed the principal cause of their failure. The engine and fire-rooms of ocean steamers and war-vessels are exposed to temperatures of 120° to 140° F. for months at a time, and many times in succession in atmospheres heavily charged with moisture and other vapor, without any material disturbance to the protective character of the coatings.

There are commercial paints in extensive use, subject to temperatures of 300° to 350° F. under pressures of steam, which preserve their integrity after years of exposure. In these instances the life of the coating depends quite as much upon the vehicle as upon the pigment.

CHAPTER XXXI.

PAINTING BY SPRAY.

PAINTING by spray or the air-brush has lately come largely into use; in fact, it would have been impossible to have covered, in any acceptable manner, the World's Fair Buildings erected since 1890, without the use of the paint-spray process.

At the Columbian Exposition, the results of the spray method of painting, compared with the use of the hand-brush, were: A corps of hand-brush painters, working in the usual manner of applying kalsomine, averaged about 800 square feet of surface daily, while 16,000 to 20,000 square feet were covered by a spray-machine in eight hours, 30,000 square feet having been reached under favorable conditions. In the Manufacturers' Building, with a daily average of thirty men using spray-machines, at the end of eighteen working days, 1,332,700 square feet of surface had been covered; equal to an average of 2368 square feet per day per man. This was during the coldest days of winter, when the water paint, in attempting to spread it by hand, froze solid. The spray required about twenty-one gallons of kalsomine against twenty gallons by the brush, but the saving in labor was nearly twenty to one in favor of the spray process.

Gas-holders in duty are exceptionally hard to paint. One painted by spray, using iron-oxide paint, averaged from 2700 to 2900 square feet of surface per hour for three men using two sprays. The amount of paint used was not notably more than with the brush. The cost of the labor was less than ½ cent per square yard.

In the *Michigan Engineers' Manual* for 1897, Mr. J. J. Huber describes an extemporized spray-machine, and the results in painting 100,000 square feet of rough hemlock siding with iron-oxide and raw-oil paint.

The contractor's bid for labor, ladders, and brushes, the company to furnish the paint, was	35 cents per 100 square feet
The company to furnish all the material	28 " " " " "
A lump bid for the labor alone	30 " " " " "

The mill company built a spray-machine for twenty dollars, and the result of its use was, that one gallon of paint covered 150 square feet of rough-board surface. Two men covered 5000 square feet per day. Cost of the paint applied, ten cents per 100 square feet. Cost of the paint, labor, and apparatus, fifteen cents per 100 square feet, or less than one-half that of painting by hand. The paint could be applied from eight to ten feet above the spraymens' heads, and ordinary laborers could do the work.

FIG. 41.—Field spray apparatus at work.

In some experiments made by the P. & L. E. R. R., using a spray apparatus for painting box freight-cars, the time required was thirty minutes per car; one man with an eight-inch brush following the spray thirty minutes more, or total of one hour per car for each coat. To paint a 60,000-pound-capacity coal-car required two men twenty minutes each, spraying the lettering not included.

At the Master Car and Locomotive Painters' Association, in 1897, Mr. H. G. MacMasters, M.C.P.I.C.RR., reported the comparative time and costs in detail of painting box freight-cars by brush and spray.

	With the Brush.		With the Spray.	
Work Coated.	Time.	Cost.	Time.	Cost.
Sills, one coat	20 min.	$0.05	13 min.	$0.03¼
Edge board, one coat	40 "	0.10	17 "	0.04¼
Body, three coats	7 hrs.	1.05	84 "	0.21
Puttying up	1 "	0.15	1 hr.	0.15
Roof, two coats	30 min.	0.07½	12 min.	0.03
Trucks, one coat	1 hr.	0.15	20 "	0.05
Blacking ironwork	25 min.	0.06¼	25 "	0.06¼
Totals	10 hrs. 55 min.	$1.63¾	3 hrs. 51 min.	$0.57¾

Result 1.98 to one in time, and 2.82 in cost, in favor of the spray.

The danger to the health of the painters in the use of the spray is very marked over that in the use of the brush, whether kalsomine, iron oxides, or mixed paints are used. In the spraying of lead paints or those containing any metallic oxides the dangerous effects are greatly increased, even when the greatest possible care is used to guard against them. The fine mist-like spray is readily taken into the lungs at every respiration, and is more thoroughly introduced into the system than is possible by absorption from contact in painting by hand.

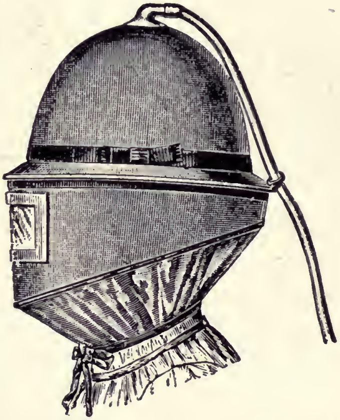

Fig. 42.—Mathewson's patent helmet for painting by spray or cleaning by the sand-blast.

The extra amount of paint, about 5 per cent, used by the spray is offset many times by the saving in labor, as above noted.

These were applications from compressed-air installations used for other purposes than painting.

The merit of oil-paint spray coatings has not been fully established. The spray necessarily carries a part of the air with the condensed moisture in it into the paint, and its subsequent escape by expansion and evaporation must result in a more porous coating than with paint applied by a hand-brush. Following the spray immediately with a brush will remove the porosity to some extent. The brushing out of any paint is a great factor in its durability, and as the use of the spray renders the employment of a cheaper grade of labor more feasible than with the use of the brush, the effects of an indifferent use of painter's "elbow-grease" will soon reveal itself in the decay of the coating.

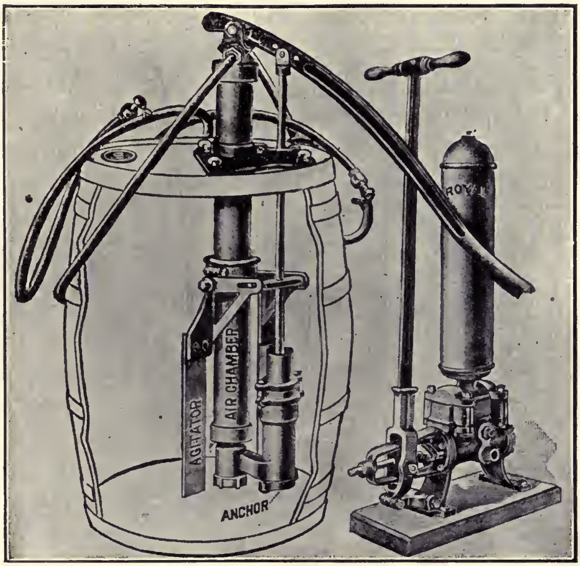

Fig. 43.—Barrel and hand-power spray apparatus.

Upon metallic surfaces the sprayed paint proves more perishable than when applied to wood.

For use in the field for repainting iron bridges, walls, and other structures there may be a saving in time of the painters, scaffolding, etc., but the work cannot be as well done as by the use of the brush. The cheaper and less responsible laborer generally employed to use the spray apparatus will neglect the necessary scraping and steel-wire brushing requisite in all repainting work, as well as the subsequent brushing out of the spray coating, particularly in the places difficult of access, where a thorough application of the paint is most necessary. Peeling of the paint and corrosion promptly follow any extended application of an oil-paint spray coating on a ferric body *in situ.*

The methods of painting were recently discussed by the Western Association of Railway Superintendents of Bridges and Buildings, in answer to a circular asking for information upon the subject. Eighteen answers were received. All were in favor of the sand-blast for cleaning either new or old metallic surfaces preparatory to painting.

Six were in favor of the air-spray for *some classes* of work, three were opposed to it, and nine were non-committal. Two who had tried it were opposed to it. One superintendent said: "On iron bridges other than on plate girders I found that there was more paint wasted than applied to the structure. The waste in attempting to paint lattice-truss work was very marked, and the coating was not equally or well spread." He favored the use of a stiff hard brush to insure a close contact of the paint, which he could not get with the spray. Too much air was incorporated with the paint by the spray, and would not release tself in the drying of the paint. It left the coating more porous than with the use of hand-brushes. Following the spray with a hand-brush did not materially help the coating in durability, when compared with surfaces spread on the same structure at the same time, by the same painters using hand-brushes, and the same paint.

"The use of the spray, following it with a heavy hand-brush, was admissible upon some of the large wooden buildings, as the failure of the paint in these cases was not attended by corrosion, blistering being the principal cause of failure in the sprayed coating on wooden and masonry surfaces."


FIG. 44.—Hand spray apparatus.

Generally, heavy or very thick oil paints cannot be successfully spread by spray, unless under air pressures of sixty or more pounds per square inch. This renders the use of the spray for oil paint useless, unless power other than hand-power is available, or the paint is applied quite hot to increase its fluidity. If the paint is thinned with benzine or turpentine to the point where a moderate pressure of air will enable the spray to work without choking in the nozzle, all of the objections to this class of paints are increased, as the extra amount of volatiles in them to be evaporated leaves the coating more porous and hastens its decay. Two coats of such air-sprayed paints are required to equal in protecting power one coat of heavy hand-brush work.

With kalsomining or water paints the spray apparatus finds an almost uncontested field, and from the great saving in labor is recommended.

CHAPTER XXXII.

MIXED PAINTS.

Reputable manufacturers of standard pigments are greatly at the mercy of many of the proprietary or patent paints ready for use that are a feature of the paint market.

Standard pigments subsequently appear in these compound paints mixed with a variety of well-known inferior substances that by some alleged special mechanical manipulation "developed in our factory" makes of them a preeminently superior product, "wholly unlike that produced by the antiquated process employed before the advent of our new idea."

Mixed paints for the great bulk of the paint trade are a convenience that cannot be ignored, and are in conformity with the general advancement of the times. Responsible manufacturers and dealers in paints furnish them; and they are more uniform in quality and color, of better composition, as well as cheaper, than when mixed by the individual painter.

Responsible paint manufacturers inspect and test the quality of all their materials, and are certain that they are standard in all respects, more than it is possible for the individual painter to do, however much he may desire to produce a good paint.

Railway companies and bridge-manufacturing firms, from the magnitude of their painted work, are able to employ the necessary staff to secure good materials, also the technical knowledge to mix and apply them. The application of the paint in a great measure is under their control, and the composition of it can be varied to meet all the conditions as they arise, and a direct responsibility established for any failure in the coating.

Failures are possible and occur with the best of paints. The hardest to locate and most annoying is where the painter, unmindful of the atmospheric conditions or the state of the surface he is at work upon, finding that the paint does not work or spread well, doses it with benzine, turps, or some other volatile or vehicle. He does not always know or care what the composition of either the paint or the added element is, so that it enables him to get through with his work without an immediate appearance of distress in the coating.

Special mixed commercial paints generally require a special order of procedure in their application, and when these are faithfully carried out will usually give better results than when the application is left to the ordinary painter's manipulation.

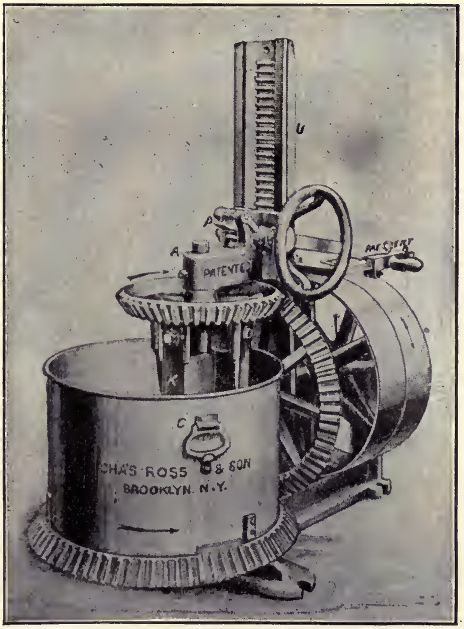

Fig. 45.—Power paint-mixer.

A few special paints that have passed the fortuitous requirements of the United States and foreign patent offices, and have one or more trade-marks to each combination, are the following:

Fire- and water-proof. Composition: coal-tar, oil, gypsum, Japan, liquid rubber, nitric acid, slate-dust, sal-soda, potash, antimony, and sodium.

Another combination of coal-tar, yellow ochre, plumbago, lime, salt, and coal-oil.

Fire and acid-proof. Composed of coal-tar, pitch, common mineral paint, hydraulic cement, gray ochre, asbestos, slaked lime, liquid drier, and litharge.

In most of the above and in other similar patent compounds the quantities of each substance are not defined, but left to the discretion of the user.

Other compounds of a kindred nature contain saltpeter, sulphur, caustic potash, mica, talc, zinc slag, salts of tartar, oxide of copper, shellac, sulphate of mercury and sulphate of zinc, verdigris, copperas, india-rubber, hydraulic-cement slag, soapstone, solutions of gall-nuts, tannin, acetone, yellow soap, lignum vitæ, garlic, asafetida, and one or more of the list of inert pigments given in Chapter XVIII.

These compounds are recommended as special paints for ferric structures. In most cases the merits are so blindly set forth that one is in doubt whether it is the preservation or destruction of the paint or the covered surface the proprietor wishes to secure.

As mentioned before, all mixed paints are not necessarily objectionable compounds, and to be avoided. A combination of pigments to secure a desired result is often necessary where the use of one pigment would be ineffective.

In the cases of red lead and lampblack the lampblack delays the setting, adds body, prevents the crawl or curdling of straight red-lead coatings, and is in every way beneficial to the physical character of the paint.

There is enough oxidizing element in the red lead to cause the lampblack (which is a slow drier) to dry without using a large amount of japan or other drier.

A small amount of French ochre is sometimes added to red-lead and lampblack mixtures to give a brighter tone to the chocolate color of the mixture, making what is called the "Pullman color." This mixture has proved to be very reliable under some severe exposures on cars.

The specifications for the painting of one of the largest bridges in the world called for a *pure red-lead* paint. Analysis of the paint *after* the bridge was painted showed that the paint contained 2 pounds of whiting and aniline color to 1 pound of red lead. This paint was completely disintegrated and ruined after only one year's exposure.

A mixture of 70 per cent of barytes and 10 per cent each of carbon black, zinc oxide, and amorphous graphite, well ground together in linseed-oil containing a small amount of Japan drier, will outwear red lead. If the coating is applied to a rusty surface, the scales of rust will break through red lead sooner than through the above mixture.

Mixtures of zinc-white and white lead, both true pigments, are thought by some engineers to be a more durable coating than either alone, and for some external exposures are said to be improved by the addition of 10 to 15 per cent of silica or barytes.

The barytes and silica in these cases, also when added to flake graphite, save oil and give weight and bulk, as well as a frictional element to hold the graphite in place during the setting of the paint.

In all these instances the paint appears to be better for the presence of the various substances; but could the same group of materials be combined into a single pigment, it would prove superior to any mechanically arranged article.

The few cases where the mixture of true pigments with each other or with an inert substance has proved to be beneficial are not numerous enough to afford any foundation for a mass of incongruous substances called "mixed paints" that flood the market, and which the reputable paint-manufacturer is almost powerless to stem. (See Chapters V–XXX.)

No reliable paint can be made without skilled labor at almost every stage of its manufacture, even with the aid of the best mechanical devices to reduce the labor account. Generally the labor and power account is two and a half to three cents per pound of paint, or twenty-five to thirty cents per gallon. Any paint worth applying to a ferric or any other structure of importance cannot be bought for forty or fifty cents a gallon. Such paint will not protect a ferric body, and if applied will prove (because of frequent renewals) more expensive than one costing three times as much.

Iron oxide is the cheapest straight pigment in use. But this cannot be *properly ground* in a reliable oil, barreled, and delivered for less than seventy cents per gallon, unless the manufacturer is losing money, or using an adulterated oil or a very unreliable iron-oxide pigment.

Mixed paints containing resin, resin-oil, coal-tar in any form, calcium chloride or sulphate, and iron oxide act as carriers of oxygen and promote corrosion; hence they are unreliable coatings.

The quality of the linseed-oil used in many of the mixed paints is against them. Oil made from unripe, smoky, condemned, or "no-grade" seeds, that often contain almost as much non-drying oil as the drying element, is too frequently used, and benzine is used for the drier instead of japan or turpentine. When linseed-oil is heated to 120° or 130° Fahr., and benzine is slowly added and well stirred, the mixture will not separate on cooling, but remain fixed until the oil is spread and dried by the evaporation of the volatile. The odor of the benzine in the paint in this case is almost suppressed; it is only markedly noticeable when the oil is again heated to near the above degree.

Hot mineral oil added to linseed-oil is hard to detect by the odor, but the character of the mineral oil as a non-drying oil is not changed in the slightest degree by the heating. A gill of mineral oil added to a gallon of red-lead paint will delay the setting of the paint. The paint never dries hard, but only on the surface. It remains viscid beneath, and the coating is liable to peel at any time.

There were sold in the United States in the year 1900 60,000,000 gallons of mixed paints and pastes, the use of which is increasing about 10 per cent each year. More paint is used in the United States per capita than in any other country. The English mixed paints are adulterated quite as much as any paints produced in the United States.

The highly extolled English "Torbay" paint is made from a 90 per cent iron-oxide pigment, and has no merit over any American brand of oxide paint containing the same percentage of iron oxide and an equal quality of American linseed-oil.

"Ferredor," an English trade-mark mixed paint, is exploited as being manufactured from a "natural metallic *steel-gray*, 95 *per cent* rustless peroxide of iron found, in a very fine state of division, as a *crystalline peroxide*, and surpasses the oxides of iron, and is superior to red lead. 'Ferredor' cannot absorb or impart oxygen, so that the oil in the paint is not destroyed, as is the case with the red oxides," etc.

The most brazen advertiser of any grade of American mineral brown paint never equalled this, and no American has been bold enough to attach to his product so fearful a trade-mark as "Schuppenpanzerfarbe."

Crosbie's paint (English) is honestly stated as being made from a 90 per cent oxide of iron, unadulterated and extra-finely ground in the best linseed-oil. Five governments and one hundred and thirty corporations show their confidence in an honestly made paint by using this firm's product, though it is but a corrosive one.

"Armour-Scale Paint" (Panzerschuppen). A Swiss ferric paint made from a number of formulæ, also one or more German paints bearing the same trade-mark, are simply iron-oxide paints made from 80 to 90 per cent iron ores that the manufacturers call "granular micaceous." A greasy, crystalline, scaly iron ore with gangue, etc. Graphite in some (unclassified) form is added and the vehicle is sometimes a linseed-oil varnish.

"Lender's Anti-Corrosive Paint," especially recommended as impervious to heat, cold, warm water, steam, volatile acids, alkalies, gaseous ammonia, hydrochloric acid gas, and sulphuretted hydrogen gas. The base of the pigment is called "a silicate of iron." It is simply an ordinary iron ore containing iron-oxide, 88.56 per cent; silica, 5.40 per cent; lime and magnesia, 3.10 per cent; alum and phosphoric acid, 0.55 per cent; undetermined substances and loss, 4.39 per cent. It is sold in the form of a paste, being finely ground in a boiled oil or varnish, and when used is reduced with raw linseed-oil, and litharge added for a drier. A special point claimed for this wonderful oxide-of-iron paint is that "any mineral paint of the right color can be added to produce the desired tone." Wonderful product! The special advantages for this special paint are accompanied by a specially high price for it.

Other examples of the foreign mixed paints and the art of advertising them could be cited. A mixed paint is not necessarily a good one because of its trade-mark and high price, nor is it a notoriously bad one because of its being an American firm's product.

Some instances of the unreliable character of compound paints have been given in Chapters V (White lead) and XXX (Paint tests). The following instance, from the cost and magnitude of the structure to which the paint was applied, the public interests at stake, and the result of the application, is of interest. It illustrates the unreliable character of compounded pigments applied over other basic pigment paints for the protection of ferric structures.

The new suspension bridge over the East River has in Brooklyn a viaduct about 9000 feet long. This viaduct is of lattice trusses and columns of the type used for elevated railways.

The steel for this structure was specified and supposed to have been cleaned by the sand-blast, but it mostly received only a coating of boiled oil before machining. After riveting up in sections preparatory to shipment it received a coating of red-lead paint, and after erection another coating of red lead and lampblack paint was applied.

After a number of months' drying the first finishing coat of Jewett's white lead, 70 to 75 parts, and the New Jersey zinc oxide, 20 to 25 parts, ground in raw linseed-oil, was applied. The engineer corps, from some previous experience with this mixture, were particular to see that the quality of all the materials was standard in all respects. The spreading of this and the following or fourth coat was *in situ* and under their eyes; hence they alone are to blame for any errors in this. After a number of months, the fifth or finishing coat, composed of the above white lead and zinc oxide mixture, also a small quantity of French ochre to make the coat cream-colored, was applied.

In a not particularly severe exposure, and in two years, the last three lead and zinc coatings were disintegrated and washed away in large areas over the entire structure, showing the foundation coats of red lead. A cloth wetted in water and wiped over the coatings washed them off as freely as though they were of whitewash. Wringing the cloth left the three coats of lead and zinc pigments in the water like so much chalk. If the percentage of zinc oxide in the coating had been forty, the paint would have failed by peeling in strips instead of chalking. The paint, in its materials, proportions, application, location, and exposure, is not far different from that of the New York City elevated railways, which thus far has kept its place free from chalking, but has not prevented corrosion from attacking every foot of the structure beyond the possibility of correction.

Had the same amount and quality of the paint been spread on a thousand inland structures, the failure of the coatings would not have been so marked as in the above case, where the agency of acres of decayed paint tells the tale; but it would have occurred just the same, though the loss would have been so widely distributed as to call no special attention to it.

The reliable qualities of a paint composed of a number of pigments, or a compound paint, where the substances of the compound are united as an individual whole by chemical affiliation in the process of manufacture, have been mentioned a number of times in this work. The annexed figure (46) illustrates the durable nature of that class of pigments.

Fig. 46.—Four-inch wrought-iron pipe.

It is the photograph of a four-inch-diameter wrought-iron pipe. The upper end, *A*, was enclosed unpainted in a cast-iron ring. The lower end, *B*, is the adjoining part of the pipe that had been painted with two coats of sublimed lead and zinc. The pipe and its connections were buried in the earth for nine years. When taken up the end *A* had corroded and lost over $\frac{1}{16}$ inch in diameter. The part *B* was uncorroded and nearly all of the paint on the whole length of pipe was unchanged and in place. Where the coating was scaled off in the process of removing the pipe from the trench, the iron was as clean and uncorroded as when laid. (See Chapter V, Sublimed Lead.)

Sir Benjamin Baker has concisely remarked that "it is the deviation from the average which really is so important in the design of engineering works."

This is equally applicable to the design of a paint. The majority of paint-manufacturers appear to harbor the idea of the universality of their product. They give little or no attention to location, exposure, or the many influences to which it may be subjected during its life on a ferric structure.

A paint that is reliable in open inland locations often fails on the seacoast, or in manufacturing towns, or on industrial establishments. The paint that is reliable in the latter place may fail quickly on another not far distant location because of disregarding one or more of the above factors.

It is important that both the engineer and the paint-compounder remember that there are a number of affinities in a paint coating. These are where the vehicle and the pigments are capable of mixing, not to form a new chemical compound, but to influence the action of one of the group; for instance, where red lead or red lead and lampblack are added to influence the drying of the paint. Another instance is where a substance combines in definite proportions, such as the carbonate of lime added to an iron oxide to neutralize the sulphur in the pigment, or the acid in the vehicle.

It is also to be kept in mind that every metal is electropositive to its own oxide; the latter induces corrosion in the former whenever the two are brought into contact, as in a paint coating. The vehicle only insulates or protects either substance but indifferently, particularly where the covered metal is the base of the oxide in the paint. The water and acids in the oil (the latter not infrequently rancid) have great influence in the decay of the coating and corrosion of the covered metal.

The production of enamel paints has become a trade of great importance. They differ from ordinary oil-vehicle paints inasmuch as they dry with a high lustre or gloss. They were first called "varnish paints," for the reason that the vehicle was a varnish, instead of linseed-oil. They are used principally for coating walls on the inside of buildings that require to be washed with water, as in hospitals, courtyards, etc., the varnish vehicle being less easily injured by the water than an oil vehicle.

The use of a varnish vehicle for ferric paints has been tried in a number of instances in late years with varying degrees of success. The principal difficulty in their use is the uncertain character of the varnish vehicle, which requires a greater knowledge of the nature of the fossil resins and how to compound them than the average paint-manufacturer has at his command.

There are three classes of enamels: *

First. The slow-drying enamels, that require from twelve to fifteen hours to dry under normal conditions. They give a fine, lustrous, level coating, and if carefully applied should show no brush-marks. They are essentially an oil and fossil-resin varnish, with which the necessary color pigments are ground.

Second. Quick-drying enamels, that dry in from twenty to forty minutes according to their composition. They are essentially spirit varnishes, colored with pigments. They leave a lustreless or flat

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* "Enamel Paints and how to use them." By Geo. W. Hurst, F.C.S. *Western Paint Magazine*, Feb. 1900, pp. 46, 47.

surface, are apt to show brush-marks, and are not as durable as the slow-drying enamels.

Third. Baking enamels. They are varnish compounds that when heated flow into a uniform and lustrous coating. The pigments added to them give them body and color. Sewing-machine and bicycle frames, hardware, etc., are examples of these coatings. In larger ferric bodies they are represented by the baked japans applied to water-pipes. (See Chapter XI.)

The composition of the varnish base of all of these enamels is the essential part, and in most cases better results can be attained if the varnish is obtained from a reliable varnish-manufacturer than where the painter makes it himself. Even the best of varnish-makers fail sometimes to produce a reliable varnish owing to many causes, principally from the use of common resin and other poor-quality gums, the effect of which is the " crazing " of the coating.

The general nature of the varnish base is indicated in the following recipes that have given good results:

Sixty pounds of good, white Sierra Leone copal, mixed with 10 gallons of the best quality of hot boiled linseed-oil. When well cooked add 16 gallons of turpentine and ½ pound of linoleate of manganese for a drier. This varnish, suitable for all colors from black to white, should be ground in as for oil paints.

A cheaper grade of varnish can be made from 35 pounds of Kauri gum and 15 pounds of Sierra Leone copal, mixed with 7 gallons of hot boiled linseed-oil and 1½ gallons of turpentine. When nearly cold, thin down by adding 10 gallons of turpentine. This will be too dark for white enamels, but answers for all other colors.

The white enamels are usually made by adding zinc-white or lithopone to the varnish. They work well. About 6 pounds of the white is required to a gallon of the varnish. Whiting and pipe-clay are detrimental; they make the coating gray, are deficient in body, and are liable to cause "peeling."

Black enamels require 4 pounds of lampblack to about 6 gallons of either grade of the above varnishes.

A quick-drying varnish base is made from Sandarac gum, 10 pounds; soft Manila copal, 5 pounds; gum benzoin, 1 pound; methylated spirit, 8 gallons; or 4 gallons each of methylated spirit and wood-naphtha. This varnish is suitable for all colors from white to black. A cheaper varnish, suitable for dark colors and black, is: Sandarac, 12 pounds; shellac, 10 pounds; benzoin, 2 pounds; methylated spirit, 12 gallons. These varnishes dry quickly. A slower-drying varnish is made from gum dammar, 14 pounds, and 3 gallons of turpentine.

For a white enamel from either of these varnishes grind in 10 pounds of zinc-white or lithopone to 1 gallon of varnish.

For a black enamel grind in 5 pounds of zinc-white, 2 pounds of carbon black, and 3 ounces of brilliant ebony spirit-black to 1 gallon of varnish.

The baking enamels are not essentially different from the first class of varnishes herein mentioned, other than that they contain more gum or resin of some quality.

A few special recipes are the following: Best grade of refined asphaltum, 70 pounds, mixed with 9 gallons of hot linseed-oil and 5 gallons of gold size. Boil until ropy, then add 9 gallons of turpentine. This is for a black coating.

The colored enamels require a better grade of varnish base, which is made thus: A good quality of Kauri and copal gums, each 20 pounds; animi, 5 pounds; melt together and mix with 14 gallons of hot linseed-oil; boil until stringy, thin with 18 gallons of turpentine, and use with any pigments to get the desired color.

A quick-drying black enamel is composed of:

D. C. shellac	60	pounds	
Gum sandarac	20	"	
Gum benzoin	2	"	
Lampblack	5	"	
Castor-oil	0.75	"	
Spirit aniline black	1.50	"	
Methylated spirit			25 gallons
Wood-spirit			2 "
Total	89.25	pounds	27 gallons

The pigments assembled with all of the above varnishes should be of the best quality, particularly the lampblack. Pulverized bituminous coal and nearly all of the so-called "carbon blacks" prove detrimental to the quality and color of the enamel. No benzine or turpentine can be added to any of the above varnishes after they have left the cooking-kettle without affecting the gloss of the enamel.

The above enamel compounds represent only a few that are put upon the market under many special names. As a rule, the protective value of all enamel paints is quite as variable as the ordinary oil-vehicle paints. A varnish vehicle does not always secure a reliable ferric coating, unless more care is exercised in preparing the surface to receive it, or in its application, than the average painter generally gives to these matters. The use of resin or resin-oils in enamel paints is as disastrous as when used in an oil paint.

CHAPTER XXXIII.

CORROSION OF IRON AND STEEL.

THE difference in the rate of corrosion between iron and steel as given by different authorities varies greatly. The reason for this is plain: the conditions of each reported rate of corrosion, whether the result of laboratory or other tests, such as exposure to weather or other corroding influences, not being similar in all respects, are therefore comparable only in a general way.

Pieces of iron and steel, both suitable for boiler-tubes, were made clean and bright, then placed in sandy loam with which had been thoroughly mixed some sodium carbonate, sodium nitrate, ammonium and magnesium chlorides. The earth so prepared was kept moist. At the end of twenty-three days the plates were taken out, cleaned and weighed. The following was the result:

Iron had lost by corrosion....................	0.84 per cent.
Steel " " " "	0.72 " "

The pieces were replaced in the earth and left for twenty-eight days longer, or sixty-one days in all. The result was:

Iron total loss by corrosion.....................	2.06 per cent.
Steel " " " "	1.79 " "

This is a rate of corrosion that would probably have caused the disappearance of the plates inside of eight years.

Experiments conducted by the Admiralty, Board of Trade, and Lloyds prove that steel corrodes much more rapidly than iron when exposed to the action of salt water; also that the commoner brands of iron corrode less rapidly than the better brands when exposed to the same influences. With steel and iron both unprotected and exposed to the same action of the weather and sea-water corrosion advanced at the rate of one inch in depth in 82 years for the steel and 190 years for the iron. When always immersed in sea-water the periods are one inch in 130 years for the steel and 310 years for the iron. When always immersed in fresh water the periods became 600 years for the steel and 700 years for the iron.

Mr. B. H. Thwait, A.M.I.C.E., reports that a bar of wrought iron unprotected, exposed to the action of the atmosphere in a manufacturing town, demonstrated that a bar of common iron one inch by four inches would be entirely corroded away in a little over 100 years.

Mr. G. Rennie's experiments in 1836 were with cubes of wrought iron, cast iron, and bronze for lighthouse purposes. The cubes in separate vessels were immersed for seventy hours in saline solutions considerably stronger than sea-water. The cast iron lost $\frac{1}{3307}$ of its weight; the wrought iron $\frac{1}{6610}$, being in the proportions of two to one in favor of cast iron. The bronze lost $\frac{1}{10000}$ of its weight, a result in favor of bronze over cast iron of three to one. The cast- and wrought-iron cubes were then placed in a strong solution of one part of muriatic acid in twenty-five parts of Thames water, and exposed for twenty-one hours. The cast-iron cube lost $\frac{1}{33}$ of its weight, the wrought-iron only $\frac{1}{258}$, being eight to one in favor of the wrought iron.

In these experiments with the same samples of each metal the results were directly contrary. The crystalline nature of the cast iron evidently favored the disruption of the crystals from their bond or loose association together; they were cast off when partially corroded, and corroded by themselves while the acid had fresh surfaces to act upon in all directions.

The experiments of Mr. Robert Mallett, M.I.C.E., on wrought iron and cast iron sunk in the sea, showed that from $\frac{1}{10}$ to $\frac{4}{10}$ inch in castings one inch thick, and about $\frac{6}{10}$ inch of wrought iron, will be destroyed in a century in clear sea-water. This is equal to fifteen to one in favor of cast-iron. Other experiments by Mr. Mallett showed that cast iron unprotected and exposed freely to atmospheric action was corroded nearly as rapidly as by the action of clear sea-water.

Mr. Kenniple, Central India Railway Company, reports that "the greatest corrosion of cast-iron piles existed close to the low-water mark, and did not extend to any considerable distance from that point." This condition he also found to exist in the wrought-iron bolts and braces. After an exposure of twenty-five years the piles were found to be in very good condition, and corrosion had only occurred in places accessible for renewals. A thin coating of mud, marine growth, and barnacles upon the immersed surfaces of the ironwork that protected them from contact with fresh supplies of water, or from the water in motion, had a tendency to retard corrosion, but when they were removed corrosive action increased at once. He concludes that after a life of from thirty to fifty years cast-iron structures exposed to sea-water can only be regarded as of a temporary character, especially those of light cast-iron pile design.

Dr. Grace Calvert, F.R.S.,* experimented on a number of gray cast-iron cubes made of Staffordshire cold-blast iron immersed in acidulated water. The specimens were 0.39 inch cube, specific gravity 7.858, weight of cube 237 grains. The cubes were placed separately in bottles holding about 30 cubic inches of greatly diluted sulphuric acid. Similar cubes were placed in bottles containing dilute hydrochloric, acetic, and phosphoric acids. The action of the acids on the iron was slow; but at the end of three months, although the appearance of the cubes had not changed, some of them, especially those immersed in the solution of acetic acid, had softened so that a knife-blade could penetrate them 0.11 to 0.16 of an inch.

The solutions of acids mentioned were replaced by a fresh one in each bottle every two months for two years. Changes were then found to have taken place in all of the cubes, the acetic acid showing the greatest decomposing effect, then the hydrochloric, sulphuric, and phosphoric acids; the latter had the least effect upon the cubes.

The action of the acids upon the iron had changed its nature, without any alteration of its bulk or in the appearance of the surface of the cubes. The weight of one cube after two years' immersion was 54 grains against its original weight of 237 grains. Its specific gravity was 2.751 instead of 7.858. The change in the physical character of the iron is indicated by the following analysis of the gray cast-iron from which the cubics were made, and a set of cubes after a two years' immersion in the acetic acid solution:

	Before Immersion.	After Immersion.
Iron.	95.413 per cent.	79.960 per cent.
Carbon.	2.900 "	11.070 "
Nitrogen.	0.790 "	2.590 "
Silicon.	0.478 "	6.070 "
Sulphur.	0.179 "	0.096 "
Phosphorus.	0.132 "	0.059 "
Loss.	0.108 "	0.155 "
	100.000	100.000

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* Minutes of Proceedings of the Institute of Civil Engineers.

Dr. Angus Smith found that, taking the inland country parts of England as a basis for the acidity of rain-water and the impurity of the atmosphere, and rating them as 0, in Glasgow they were 83, and in London 28.

The comparative amounts of ammonia and other impurities in the air and in rain-water were: Valentia 1, Glasgow 50, Liverpool 30, Manchester 36. For the amount of hydrochloric acid present in the same elements Blackpool was 100, London 320, the Underground Railway in London 974. Anhydrous sulphuric acid at Blackpool 100, London 352, Underground Railway 1554. Ammonia and albuminoid ammonia at Innellan, on Firth of Clyde, 100, London 108 and 117, Glasgow 150 and 221, the Underground Railway 138 and 271.

Drs. Clowes and Andrews' examination of the air in the cars of the Central London Railway showed a maximum amount of carbon dioxide of 14.7 volumes and a minimum amount of 9.6 volumes in 10,000 volumes of air. In a railway-station elevator 15.2 volumes was found.

Many points in the Paris underground railway system have 33 volumes of carbon dioxide in addition to other deleterious gases and 2 per cent of aqueous vapor. Dr. Clowes states that not more than 8 volumes of carbon dioxide in 10,000 volumes of air should ever be present at any point in a railway building.

Dr. Smith also found a variety of solid substances in the air, such as common salt, sulphur, nitrate of ammonia, lime salts, iron; also the phosphates, iodides, and other organic matters given off by animals, vegetables, etc. The percentage of oxygen in the open air varied from 21.0 to 20.40, while the carbonic gas varied from its normal amount of three parts in ten thousand to over thirteen parts in the London Underground Railway, and some parts of the Swiss tunnel contained over 17 per cent.

Dr. Huxley's Physiography gives his examination of the amount of carbonic acid gas in 10,000 parts of the atmosphere at a number of points as examined by him, viz.:

On the River Thames at London, mean	3.43
In the streets of London "	3.80
Top of Ben Nevis, Scotland, 4436 feet high, mean	3.27
A ward in St. Thomas' Hospital, London	4.00
Haymarket Theatre, London, Dress Circle at 11.30 P.M. when lighted by gas	7.57
Underground Railway, London	14.52
Average of 339 English mines	78.50
Highest amount in a Cornish mine	250.00

See Chapter XXXVI for corrosive elements in snow-water.

Dr. W. G. Black * gives the results of his examinations for dust and soot in the air, in the central district of Edinburgh during the year 1902. The fall of dust and soot in an open dish of 75 square inches area amounted to 2 ounces, equal to 3.8 ounces per square foot, or 23.5 pounds for every 100 square feet.

The above amounts of corrosive elements are not arbitrarily constant, but they indicate the corrosive influences that may be encountered in almost every situation of engineering work.

Mr. Beardmore, C.E., instances a case of a sea-lock, in which soft water was "locked" down into the sea-water level. At the end of thirty-five years' service all of the cast- and wrought-iron attachments to the wooden lock-gates, also the spikes in the platforms and gate-sills, had completely corroded away, though the timber parts of the structure were perfectly sound.

Ferric metal exposed to the action of salt or fresh water which is not changed corrodes far less rapidly than where the water is changed more or less frequently.

Dr. Lyon of India, a high chemical authority, reports that some cast-iron piles, after four and a half years' exposure to the action of pure sea-water having a specific gravity of 1.028 and that contained 3000 grains of solid matter per gallon, of which 1605 consisted of the chlorides of sodium, magnesium, etc., had undergone a change to a depth of $\frac{1}{10}$ inch from the surface of the metal.

The Milton-on-Thames pier was erected in 1844 on cast-iron columns 3 feet in diameter and 1½ inches thick. In the Gravesend town pier and the Maplin Sands lighthouse the cast-iron columns and other cast-iron members exposed to the sea-water were originally 1¼ and 1½ inches thick. In all of these structures, at the end of forty-five years, only ¾ inch of the metal remained unaffected; the rest had changed to the semblance of plumbago. None of the members of these structures indicated any change in the metal.

Mr. Thomas Rhodes, C.E., reports that "in the locks of the Caledonian Canal the cast-iron sluice-gates were exposed to sea-water. All of the parts were coated with a heavy Swedish tar, except on the working faces of the gates. These faces were faced and ground together. Four years after the immersion of the gates. upon an inspection of their condition, on all of the parts coated with the tar no corrosion was apparent, while the machined and ground

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* Royal Meterological Society Journal, XXII, 1903, p. 134.

working faces were softened and changed to plumbago to the depth of ¾ of an inch, and had to be renewed."

The experience of American engineers appears to be equally conclusive of the treacherous character of cast iron exposed to sea-air or sea-water.

Mr. John D. Van Buren, in a paper read before the American Society of Civil Engineers, stated that "bolts and other wrought-iron parts are badly corroded in less than twenty-five years when submerged in sea-water. Certain kinds of cast iron could perhaps be made to last fifty years, which would be a generous allowance, and probably greatly exceeds the average life of cast iron exposed to sea-water."

Sir Benjamin Baker, in his paper "The Metropolitan and Metropolitan District Railways," * says: "In tunnel constructions when the roof members and bottom flange of the girders, tie-rods, anchors, etc., are much exposed to corrosive influences, wrought-iron members were used and thought to be more trustworthy than cast iron, but were found to be exposed to a greater risk from hidden oxidation. Experience has shown the trouble and cost of maintaining ironwork exposed to atmospheric corrosion in an underground railway. It is so great that it would justify a considerable increase in the first cost by substituting brickwork and deep cuttings for ironwork and shallower construction. Where the depth was sufficient for an arch, brick covered ways were to be preferred to iron-girder constructions, on account of the smaller cost, increased durability, and safety."

Sir John Fowler confirmed Sir Benjamin Baker's views in regard to the substitution of brick work and masonry for ironwork in all cases where possible, even at a material increase in the cost of the work. He thought the question was not confined to the relative rate of corrosion of cast iron, wrought iron, or steel, but to the great risk arising from hidden oxidation on important members of *walled-in* ironwork.

These views are corroborated in the experience of American railways. The Pennsylvania Railway has already replaced a number of its iron bridges with masonry arches, and wherever possible will continue the substitution.

Car-wheels made from the best of gray cast iron when immersed either constantly or alternately wet and dry, in fresh or salt water in all stages of impurity are found to corrode faster in the body part of the wheel than in the tread or chill, the iron being identically the same

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* Minutes of Proceedings of the Institute of Civil Engineers, Vol. LXXXI.

in both parts of the wheel and under the same corrosive influences. The difference must be attributed to the effect of the chill, which has changed the molecular formation of that part of the wheel, making it more dense and of a needle-like or filamentous formation, that is not so readily attacked by corrosion as the crystalline part. This effect in car-wheels is the more noticeable as the body part of the wheel is covered with a skin of the silicate protoxide of iron, produced by the molten metal fusing the sand in the mold. There is also a further protection afforded by a film of the black magnetic oxide of iron being formed at the same time by the oxidation of the hot metal in cooling.

Cast-iron pipe or piles would be more durable were they cast from chills the same as the tread part of a car-wheel. Instead, however, of this method, which is attended with some difficulties not present in the casting of car-wheels, it has been proposed to increase the depth of the silicate coating on such bodies by a process used by the late Mr. E. F. C. Davis, late President of the American Society of Mechanical Engineers, in the protection of mining pumps, chambers, and pipes subject to the action of mine-water. The corrosive action of this fluid is very great and increases by motion and pressure. The process consists of coating the cores and other parts of the mould with a thin paste applied by a brush, which increases the thickness of the silicate coat to more than double its natural thickness, and can be made still thicker by repeated applications of the paste before casting. The composition of the paste is, viz.:

112 parts silica.
44 " calcined soda carbonate.
24 " " carbonate precipitate.
4 " boracic acid.

Mix and thoroughly pulverize them. Coat the core or mould with plumbago facing, and apply the enamel as a powder or paste to the thickness required, in one or more applications, and cast as usual. A single coating with this compound more than doubles the life of the metal.

Fresh or sea water impregnated with decomposing organic matter, or acids and chlorides discharged from bleacheries, paper-mills, etc., hastens corrosion, which is increased by motion, pressure, and high temperature.

The Merrimac River, at Lowell, Mass., is affected to such an extent by the discharge waters from manufactories, that during the ordinary flow of the river in summer, it will change litmus paper.

Instances are on record where firm gray cast-iron water-pipes of large diameter and 1 inch in thickness, conveying sea-water, have inside of five years changed to a plumbago-like substance, that had hardly any strength and could be cut easily. No change in the appearance of the metal was indicated; the change in the metal was from the inside, or where in contact with the water. The pipes had the usual tough skin, and were nominally protected by a foundry dip coating.

Mr. F. A. Boyer, M.E.,* reports that a cast-iron water-pipe 12 inches in diameter, 1200 feet long, used to circulate sea-water for condensation purposes, laid mostly in the open air, was changed in two and one-half years to a plumbago-like substance that could be cut easily, but to the eye presented no indications of the change in the metal.

Gray cast-iron water-pipes † laid at Atlantic City, N. J., for nineteen years, in black swamp-mud containing decomposed vegetable and saline substances highly acidulous and corrosive, were found to be generally corroded externally. The iron was softened about $\frac{1}{8}$ inch in depth, and in many places it had extended through the pipe. The corroded metal appeared to have been replaced by a clay-like substance of light weight, containing 17 per cent of silica, particles of the cast iron being embedded in it.

A member of the American Water-works Association reported in the 1902 meeting the decay of two cast-iron suction-pipes, where the metal was changed to a graphitic substance, easily cut. The suction water was originally soft ground-water, but later was artesian well-water, containing a small amount of sulphuretted hydrogen. Wherever brass and iron came in contact with the water-mains, eventually the iron became soft enough to cut easily.

Mr. Trautwine, an eminent American civil engineer, recommends a white close-grained cast iron or chilled iron for piles and wharfs exposed to sea-water or sea air.

Mr. Turner, Assoc. R.S.M., recommneds a gray cast-iron for docks and piles exposed in English sea locations.

The above results of the use of different brands of cast iron for sea-air and sea-water exposures in different locations are probably due to the difference in sea-water in different parts of the world. Sea-water varies greatly in corrosive and fouling properties even if not contaminated as mentioned before.

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* Transactions American Society of Mechanical Engineers, Vol. XVI, 1894. Paper No. 626, p. 416.

† Prof. W. P. Mason, Troy Polytechnic Institute, Troy, N. Y.

Cannons and other tough cast-iron articles, 6 or more inches in thickness of metal, sunk in the sea in many parts of the world, change in about one hundred years to a soft carburet of iron or a plumbago-like substance, without any diminution in size or any exfoliation in scales or flakes, as in atmospheric oxidation. They become too hot to handle, when first raised and exposed to the air, from the absorption of oxygen.

Mr. Francis T. Bowles, Naval Constructor United States Navy, states: "That the corrosion of iron and steel, from the observations made at the different Government navy-yards, with the different kinds of iron and steel used in naval vessels exposed to sea-water in various parts of the world under a great number of conditions of temperature, brackish, sewage, and dock water, was: That unpainted iron and steel plates will corrode in one hundred years on each exposed surface .30 to .50 inch of metal; in ordinary fresh water, .02 to .03 inch, and in the atmosphere, .25 to .30 inch." But he makes no distinction in the rate of corrosion between iron and soft steel.

Mr. L. M. Hastings, City Engineer, Cambridge, Mass., reporting the results of his experiments to ascertain the difference in corrosion between wrought iron, soft steel, and cast iron, all uncoated, exposed to a running mixture of pond and brook water, fairly soft and comparatively free from any acid or saline matters, states: "That after an exposure of one year the uncoated wrought iron was badly tuberculated and rusted, the soft steel was similarly affected, but not to the same degree; the cast iron was also affected. The percentages of increase in weight due to corrosion were as follows: The wrought iron, 1.5 to 3.1 per cent; the steel, 1.1 to 2.1 per cent, and the cast iron, 1.0 to 0.96 per cent. A similar set of plates buried in sand, also in clay soil, showed the same relative difference in corrosion of the metals."

Dr. Robert H. Thurston* reports the result of his investigations of the different rates of corrosion between iron and steel. Briefly, they are: "Cast iron in dilute solutions of acids is rapidly acted upon, the metal retaining its general appearance unchanged. The condensation waters from engines are strongly corrosive. Hard iron, rich in combined carbon, rusts slowly. Graphitic iron, also different qualities of iron in contact, increases the rate of oxidation presumably by forming local voltaic couples. Hard steel

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* "Materials of Engineering," Sec. 192, Vol. II, pp. 328 *et seq.*

rusts less rapidly than soft steel. Bilge-water corrodes iron and steel rapidly. Iron ships carefully painted have been found to corrode at a rate not far from $\frac{1}{16}$ inch in twenty-five years." 3

Thwaite* gives a formula and table of constants for the rate of corrosion between different metals under different elemental exposures, all for unprotected metal, viz.:

Material.	Water.				Impure Air.
	Sea.		River.		
	Foul.	Clear.	Foul.	Clear Water, or in Air.	
Cast iron.	0.0656	0.0636	0.0381	0.0113	0.0476
Wrought iron	.1956	.1255	.1440	.0123	.1254
Steel.	.1944	.0970	.1133	.0125	.1252
Cast iron, no skin. . .	.23	.0880	.0728	.0109	.0854
Galvanized iron. . . .	.09	.0359	.0371	.0048	.0199

Average for sea-water: Cast iron, in contact with brass, copper, or gun bronzes, 0.19 to 0.35; wrought iron, in contact with the same, 0.3 to 0.45.

No analysis of the constituents of the several metals is given, and the terms hard and soft metal are very variable conditions. However, all of the above experimenters give hard metal, whether of cast iron, wrought iron, or steel, as being less corrosive than soft metal.

Mr. Thomas Andrews, F.R.S., experimented at the Wortley Iron Works on wrought-iron and steel plates containing varying amounts of carbon. The plates were immersed in sea-water that was changed monthly. It was found that the lower the percentage of combined carbon in the metal, the lower was the corrosion. The best wrought iron corroded less than any of the steels at any stage of their exposure during the one hundred and ten weeks of the test. Wrought iron that contained double the usual amount of phosphorus and manganese corroded more than the iron free from these substances, but the corrosion in them was less for the whole period of the test than in any of the steels, with the single exception of a very soft Bessemer. 3

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* *Engineering News*, Nov. 3, 1898.

In any of the steels, manganese in excess tended to produce an increased corrosion, evidently from its unequal distribution and the galvanic action on the adjacent metal.

On the whole, from the many reported cases of corrosion in all parts of the world, that include many qualities of cast iron and wrought iron that have had approximate exposures for thirty or more years, it appears that hard close-grained and chilled iron are less liable to corrode than any brands of softer metal. Bessemer, open-hearth steels, also steel castings used for structural work, have not yet had time enough to afford many comparisons with each other, or with cast iron and wrought iron, to prove which metal is the most affected by corrosion.

It is left to the future to develop some alloy of iron or steel that will retard if not prevent corrosion, while not materially reducing their strength or other qualities.

The composition of wrought iron and the processes it is subjected to between the bloom and finished article have a great effect to determine its rate of corrosion. Iron containing sulphur is red short, that containing phosphorus is cold short. Both differ in corrosibility; the cold short is the one less affected, being harder and more crystalline in composition, while the red short has the sulphur element to aid corrosion. Neutral iron made from both of the above brands has a different rate of corrosion than either.

The same quality of iron worked in the rolls, in the one case both lengthwise and crosswise, to produce sheet or plate iron, differs in corrosibility from that worked principally in one direction, as in the case of beams, angles, and other structural shapes. All of the latter forms tend to disintegrate by corrosion into strips, needle or fibrous form, owing to the granular character of the iron being changed by the rolls into parallel fibres, that are not interlocked as the cross-rolling arranges them. The corrosion aided by the cinder follows the grain of the metal. The cinder is acid and porous, and only in mechanical bond with the iron by reason of the action of the rolls.

Fig. 47 shows the effect of laminated corrosion of a steel-plate girder on the Washington Street railway bridge in Boston. Wrought-iron pipe used for water, steam, and gas service is an example of this make of iron. It corrodes more rapidly than the same quality of iron in bars. The iron is not so condensed in the process of rolling a tube as in rolling a bar. The tube skelps receive their principal rolling lengthwise, while bar iron gets some edge-rolling in passing through the rolls. Enough, in fact, to show a marked difference in the corrosion of the two products, when from the same metal. Boiler-tube skelps, being made from a better quality of iron, or having been refined by a further working of the same grade of metal, by having had some cross-rolling before being made into skelps, are less affected by corrosion than ordinary wrought-iron pipes. The arger sizes of these pipes being made from long rolled skelps and lap-welded, instead of only welded, as in the case of small pipes, show in the welds a less corrosibility than in the body part of the pipe. This is due to the additional condensation of the fibres at the welds; also there is less cinder in the lap-weld.

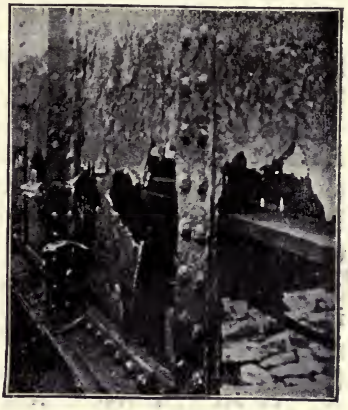

Fig. 47.—Laminated corrosion of a steel-plate girder on the Washington Street railway bridge in Boston.

Cold-rolled shafting and rods are rendered more dense by the rolling process, and they are less affected by corrosion than the bars from which they are cold-rolled. The process also increases their tensile strength. Cold-drawn wire also presents the same features. A wire nail corrodes less than a cut nail, so does a hammered or so-called wrought nail.

Polished iron and steel tools, sword-blades, razors, etc., resist corrosion better than the same articles ground, but not polished; the improved resistance being due to the surface not having so many small cavities to hold any moisture reaching it, because of the condensed and repellent nature of the surface due to the polishing.

Burnished surfaces resist corrosion and are more repellent of moisture than polished ones; but, if corrosion is once established on them as a spot, it appears to concentrate an energy to produce a deep corrosion, that is difficult to eradicate.

Rivets have a different rate of corrosion between their heads, or points, than the body of the rivet. Corrosion of a riveted joint generally concentrates its action more immediately around the rivet heads and points, than on them, forming a pit or seam furrow. A number of disastrous failures of important ferric structures have occurred from this type of corrosion.

The quantity of metallic iron in the best refined brands is 99.8 per cent. In common bar iron it is 98 to 98.3 per cent. In ordinary cast iron, about 93.5 per cent, and 2.5 per cent of graphitic carbon.

The porosity of volume in ordinary cast iron is 1.41 per cent; in different kinds of Bessemer steel, 0.41 to 1.20 per cent. In a locomotive tire ingot, 0.57 per cent. For a hard iron tire, 0.97 per cent. In a basic-iron rail ingot, 1.95 per cent. In a basic-steel ingot, 1.22 to 2.17 per cent.

At an annual convention of the American Institute of Architects, in a discussion on the use of iron and steel in the construction of modern high buildings, it was reported by one of the leading architects in the United States that the iron beams removed by him from the old *Times* building, though in use only thirty-five years, were rotten with rust. They were enclosed in eight inches of brickwork, forming the arches that supported the pavement over the vault where the steam-boilers were placed, and though always dry, yet had been exposed to ordinary fire-room vapors. They had been well painted with iron-oxide paints and protected from external moisture by an asphalt covering. The iron came off in strips, clearly showing that the rust had followed the lamination of the iron, the web of the girders being so rotten as to be easily broken by the fingers. Other examples of sidewalk beam corrosion are given on page 269.

Anchor-stocks made from hammered iron always show less corrosion than cable links. In both cases only the best quality of iron, that contains but a small quantity of cinder, is employed. The link corrosion is in the form of strips, following the fibre of the metal, while the anchor-stock generally corrodes in a compact scale form. A different rate of corrosion exists in the cable links at the end, where they are welded from that shown in the body. The iron in or near the weld is refined and more dense, also has the fibres interlaced; all these points have a tendency to delay corrosion, which is more rapid where the fibres are undisturbed by the hammer.

Tunnel Shields and Submarine Metal Corrosion.

With the recorded instances of the corrosion of iron and steel to judge from, it may be pertinent to ask, how long will the metal lining of submarine tunnels last? Notably, those laid in sea-silt or ocean mud. The integrity of the brick lining is wholly dependent upon the metal shield put in place as the work progresses, and without which the construction of the tunnel would be impossible. Even when completed, these constructions have a small margin of strength above that necessary to get the metal into place during construction, and none at all as a reserve for the loss in strength from the inevitable change in the metallic work exposed to sea-water, which begins just as soon as the shield is in place; and in the case of tough close-grained cannon metal, has been ascertained to be at a rate of about six inches in one hundred years.

Fig. 48.—Corrosion of a steel plate from the Washington Street railway bridge in Boston.

The lining plates and ribs for tunnel-shields are seldom over three inches thick. The different sections of the shield utterly preclude any material strength to be derived from their circular form, made with bolted joints. The bolts holding the shield sections together and to each other are relatively small, and will be the first to yield to the effects of saline corrosion.

The brickwork or concrete lining of the tunnel, however thick, or the thin coat of partly dried paint, will not protect the shield metal, for any appreciable time, from the change to a plumbago-like substance, which does not require the presence of air to produce it. The passage of railway trains through the tunnel will set up an undulating or vibratory movement through the tube resting on its bed of salt silt, like a log of wood in a mill-pond, being hardly more resistant to a change of position from any force, and relatively not a hundredth part as strong.

However strong such metallic shields and masonry-lined constructions are when driven through rock or earth, in or through salt water or the saturated silt of salt water, they are the most treacherous and dangerous of all engineering devices yet conceived, affecting the transportation and safety of the public.

Metallic salts and acids in water intensify the corrosion of all metals exposed to their action either by immersion or by condensation of the vapors from them. The metal-work of railway tunnels is disastrously affected by the condensed vapors of sulphurous and carbonic acid and the moisture due to such locations, the corrosion of the metals decreasing the resistance of the water to voltaic circuits; this corrosion by liquids being voltaic phenomena in all cases, and in many cases is intensified by the moisture being in the form of drops instead of being uniformly spread over the whole surface.

The cut (Fig. 49) from the *Railroad Gazette,* November 23, 1894, represents a section of a seventy-six-pound tee-rail laid in the Musconetcong Tunnel, removed after being laid five years, having lost more weight by corrosion than wear. The dotted lines show the original size of the rail, and the full lines its present worn and corroded size, which is very marked. The rails were removed on account of their strength having been seriously affected by the corrosion. The tunnel is very damp, and a great deal of sand is used by the engines, which kept the base of the rail covered, the vibration caused by the passage of the trains having a tendency to remove the thin scale of rust almost as rapidly as it could be formed. There was but little apparent difference in the corrosion, whether between the cross-ties or where the rail rested upon them. The flanges of the wheels removed the rust as it formed on the side and top, leaving a clean surface that would sensibly corrode between the intervals of the trains.

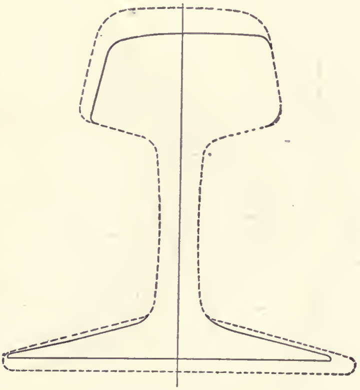

FIG. 49.

In the St. Gothard Tunnel, 49,168 feet long, the air remains almost motionless for twelve hours per day, and though the accumulation of carbonic acid is rapid, and a part of it is absorbed by the great quantity of water present, the air is almost unrespirable, and causes a great deal of distress to the workmen, and the corrosion of all metal-work inside the tunnel is very rapid.

The water that trickles down the walls of the tunnel is the condensation of the exhaust gases from the locomotives. It contains sulphuretted hydrogen, sulphur dioxide, ammonia, and carbon dioxide, and other combustion gases. The rails are renewed every ten years, and the telegraph cables in the tunnel require exceptionally strong wrappings.

In the new Simplon Tunnel, 64,718 feet long, forced draft is proposed, requiring over 500 H. P. at the ventilator shaft. The fans render an effective duty of 65 per cent, 1760 cubic feet of air per second being required for ventilation.

In general, the corrosion of metals in tunnels where the rails are bedded on cast-iron chairs is represented by cast iron, 100; wrought iron, 129; steel, 133.

In the Arlberg Tunnel, 33,587 feet long, the corrosion of the rails and other metals is so rapid, that they all require renewal every ten years. The corrosion comes principally from the condensed gases of the locomotives, though the traffic is light and a good quality of coal is used. The temperature of the tunnel remains almost uniformly 75° F. throughout the year.

The amount of free sulphuric acid in the exhaust gases from tunnel locomotives using a good quality of bituminous coal has been found to be about 5 pounds per hour, varying from -0.3 to $+7.9$ per cent.

In a tunnel in France 2850 feet long, where but little water came through the walls, the 78-pound-per-yard rails were replaced after the passage of 230,000 trains at a speed of nineteen miles per hour. They had been eleven and one-half years in service and had lost in weight $18\frac{3}{4}$ pounds, or 24.166 per cent per yard. The corrosion was general over their whole surface, but the rolling action of the wheels on the head increased the corrosion at that point by keeping the metal bright and removing the rust as fast as it formed.

Rolled-steel cross-ties for the Indian State Railway, laid in soil that was not actively corrosive, at the end of ten years had not corroded to any greater extent than the rails laid on them.

In other locations where steel cross-ties were embedded in soil containing sea-sand and saltpetre, both highly corrosive, the rails and cross-ties were heated to 300° F. and immersed in a hot bath of 3 parts of coal-tar pitch and 1 part of petroleum dead oil. This coating was firm and tough, and did not flake or scale off in transportation or in the laying of the rails. At the end of twenty years the metal had not corroded to any appreciable extent, except where mechanically injured. This coating was practically the coal-tar dip used on water-pipes by English founders.

Mr. Otto Herting cites the instance of the corrosion of some tee-rails used as girders in a Cape Breton mine, that had been abandoned twenty years. The metal was changed to a grayish-brown color, could be cut, and had a specific gravity of only 2.053. The metal powdered in a mortar was magnetic. It analyzed as follows:

Iron	31.50	per cent.
Graphitic carbon	24.10	"
Silicon	14.20	"
Manganese	1.93	"
Sulphur	1.00	"
Phosphorus	5.85	"
Undetermined and loss	21.42	"
	100.00	"

Fig. 50 represents the corrosion of steel rails laid upon docks and other places contiguous to sea-water, where the effect of corrosion was equal to about 4 per cent each year upon the weight of a 32-pound rail per yard. The details of the rail from which the cut was made were contributed by Mr. Delprat, Chief Engineer of the Sumatra State Railway, through Mr. J. W. Post, Divisional Chief Engineer of the Netherlands State Railway.

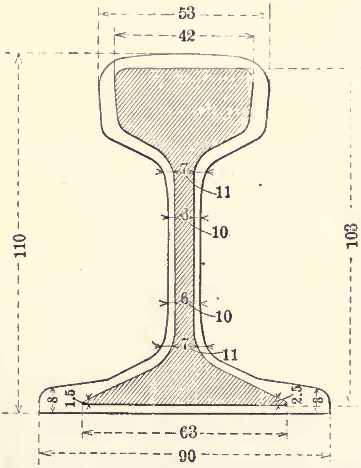

Fig. 50.—Rail section of the Sumatra Railway, showing the effect of corrosion by sea-water in ten years.

The annual report for 1900* of the Samarang-Joana Steam Tramway Company (of Java) states that a considerable number of steel rails had to be removed from the harbor tracks on account of corrosion, which amounted to 10.7 kilos per meter.

Mining metal is exposed to se-

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* *Engineering News*, November 21, 1901.

vere corrosion from many sources, the presence of sulphurous water from decomposed pyrites and other minerals, aided by heat, intensifying the action.

Thermo-electric currents arise from changes in temperature and set up voltaic action which, though slight and not easily detected, will enlarge all fissures, cavities, and seams sufficient to sap the strength of the metal.

Dr. Henry Wurtz * proposes an electro-chemical process for protecting mine metal, by connecting all of the fixed metal in the mining plant as the negative element, with a dynamo of sufficient force to overcome the galvanic energy of the surfaces when exposed to the mine's corrosive liquids, the positive terminal to be connected to a mass of hard coke in the mine sump. These conditions vary but slightly from those existing in a ship, and it is not improbable that both systems could be made to work effectively.

In a number of instances where the whole system of mining-pipes required renewal every two years, corrosion was completely stopped by coating them with an enamel in the following manner:

The pipes were first pickled in a bath of hydrochloric-acid solution to free them from the foundry scale, then washed thoroughly, and dried. The pipes then received a coating of 34 parts of silica, 2 parts of soda, and 15 parts of borax. These were mixed in a little water and the pipes exposed for ten or fifteen minutes in a dull red-hot retort. A second coating was applied, composed of 34 parts of feldspar, 19 parts of silica, 24 parts of borax, 16 parts of oxide of tin, 4 parts of fluor spar, 9 parts of soda, and 3 parts of saltpetre. These were melted together in a crucible. When cold the mass was ground to a fine paste in a little water and applied to the pipes with a brush. The pipes were then exposed in a muffle to a white heat. The enamel so formed thoroughly united with the iron, and has protected the pipes for over forty years, and they are apparently in a good condition now.

The Journal of the Society of Chemical Industry (London), February 28, 1894, details some experiments upon the galvanic action of sea-water upon iron and steel structures in various relations with each other, as constructive parts of trusses, boilers, etc., to prevent the corrosion. The use of zinc and other easily oxidized metals and alloys is suggested, to be so placed and connected to the

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* "Preservation of Metals from Corrosion by Electric Polarization." *Engineers' Magazine*, Vol. VII, No. 3, May, 1894.

structure that they will form the electro-positive element of the ever-present galvanic circuit, and by their decomposition protect the structure, or at least aid the paint coating in its mission of protection.

These protective features, proposed for the internal parts of a ship, do not apply to the protection of the external surfaces, where an entirely new set of conditions are in force, owing to the numerous rivets employed to hold the plates together and to the frames, and which are necessarily unprotected from the many sources of corrosion herein mentioned.

Professor V. B. Lewes * of the Royal Naval College, Greenwich, England, at a recent meeting of the Institute of Naval Architects, London, states:

"The rusting of iron and steel is a definite chemical process, due to the conjoint action of air, moisture, and carbon dioxide upon the metal. The increased rate of chemical corrosive action due to a local increase of temperature is noticeable, and may be due to galvanic action set up between portions of the same metal at different temperatures.

"It is an undoubted fact that the double bottom of ship plates near the boilers corrodes more rapidly than similar plates in other parts of the vessel, and the increase in temperature near the boiler is the only factor.

"It is also noteworthy that the plates at the bottom of the cellular spaces which are kept cool by contact with the sea-water do not corrode; and cases are noted in which parts of a plate, which get locally warmer than other parts—although the difference can only be a few degrees—corrode much more rapidly than the cooler portions.

"Experiments show that the rapid corrosion found in the double bottoms near the boilers or other sources of heat, is due to galvanic action, and not to the increased chemical activity due simply to the increase of temperature. As the ashes are drawn and quenched with sea-water near these exposed plates, no doubt some of the corrosion can be traced to the gases thus formed; the sulphur in the ashes also contributing its effect."

Mr. William Thomson, F.R.S., read a paper on "The Influence

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* A paper read at the thirtieth session of the Institution of Naval Architects by Prof. Vivian B. Lewes, F.R.S., F.I.C., Royal Naval College Associate, April 12, 1889; and published in full, *Scientific American Supplement*, Vol. XXVIII, No. 709, August 3, 1889; pp. 11, 320.

of Some Chemical Agents in Producing Injury to Iron and Steel," before the Manchester Association of Engineers, November 25, 1893, in which he refers to the interesting and exhaustive experiments made by Mr. Thomas Andrews, F.R.S., on the galvanic action which takes place between iron and steel, and between iron of different kinds and steel of different kinds, viz.:

"The galvanic action between wrought iron, cast metals, and various steels during long exposures in sea-water." Institute of Civil Engineers, Vol. 1883–84, Part III.

"Corrosion of metals during long exposures in sea-water." Institute of Civil Engineers, Vol. LXXXII, 1884–85, Part IV.

"The relative electro-chemical positions of wrought iron, steel, cast metals, etc., in sea-water and other solutions." Royal Society of Edinburgh, Vols. 1883–1889.

Mr. David Phillips's paper. Institute of Marine Engineers, 1890.

In the above-named articles Mr. Andrews shows that while some varieties of iron and steel remain constantly electro-positive or electro-negative to each other, others change, taking opposite positions toward each other, while others again change positions constantly during long periods, these changes always producing rust.

"It can be easily understood that while there is no material voltaic action between two pieces of steel or two pieces of iron, or of pieces of steel and iron, there may be conditions on the surface of one plate or rivet which may act strongly as an electro-negative element, and produce rusting on the metal in contact with it. A piece of iron immersed in *weak* nitric acid begins to dissolve at once. A similar piece placed in *strong* nitric acid, touching it for a few minutes with a piece of platinum wire, and then putting it into the weak nitric acid, will not dissolve, it having been rendered passive; and similarly, there is reason why one piece of iron may act electro-negatively toward another piece of the same metal, on account of some slight alteration of its physical properties, by hammering, such as closing the riveted seams of plates, calking seams, setting tubes, etc., or it may have attached to it some oxide of iron, which always acts electro-negatively toward any metal with which it is in contact, and induces oxidation in such metal."

The commission of English engineers,* appointed by the English

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* Transactions Institution of Marine Engineers (English), May 13, 1890. Minutes of Proceedings Civil Engineers (English), Vol. LXXVII, p. 323, and Vol. LXXXII, p. 281.

"Electro-chemical Effects on Magnetizing Iron." Proceedings Royal

Government to investigate the cause of the failure of the Tay Bridge, reported that where cast iron and wrought iron were connected by rivets in many parts of the same structure (as they were in this one), the rivets and connecting wrought-iron work, where connected to the cast-iron members of the structure (columns, flanges, spandrels, etc.), had corroded to such an extent as to be below the point of stability by the local galvanic circles formed at numerous points in the structure where the two metals were in contact, and the corrosion thus established was the cause of the disaster.

Mr. St. John Day, in a paper read before the Institution of Engineers and Shipbuilders, Scotland, February, 1880, stated that "the $1\frac{1}{8}$-inch diameter bolts holding the ties to the piles on the Tay Bridge were so corroded that they would have to be replaced every four to six years. Some of the bolts were found to be corroded away to one-half of their original size."

The Scotland Board of Trade now prohibits the connection of cast-iron columns with wrought-iron columns or ties.

The corrosive action noticed in the riveted sections of the tubular bridge over the St. Lawrence River at Montreal, Canada, referred to before, resembling Fig. 39, Chapter XXVIII, was of a similar nature to the above example. In this case, while the corrosion was of almost unparalleled amount and virility in the whole structure, the rivets that held the floor-beams and track-stringers in place, and were under the greatest strain and subject to vibration and shock from the passing of the railway trains, were corroded the most, though all of these parts were of wrought iron to wrought iron, but varied in quality from common iron to refined iron.

An important question presents itself to boiler-makers: whether it is safe to rivet steel plates to iron plates in steam-boilers, or even in other constructions, particularly where exposed to high tempera-

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Society, Vol. XIII, p. 429; Vol. XLIV, p. 152; Vol. XLIV, p. 176; and Vol. LII, p. 114.

"On the Corrosion of Metals in Sea-water." Minutes of Proceedings Institution of Civil Engineers (English), Vol. XLXVII, p. 323, and Vol. LXXII, p. 281.

"The Action of Tidal Streams on Metals." Proceedings Federated Institution of Marine Engineers, Vol. I, p. 191. 1890.

Report of the meeting of the British Association for the Advancement of Science, Edinburgh, 1892.

"The Wasting and Protection of Iron in Sea-water."

From "Notes on Docks and Dock Construction," by C. Colson, M. Inst. C.E. *The Practical Engineer*, London, October 19, 1893. Vol. X, No. 399.

tures or frequent changes of moderate temperatures, or to use iron rivets for steel plates or steel rivets for iron plates?

Cases are shown where furnace plates of steel riveted together with iron rivets are badly rusted or pitted in the vicinity of the rivets while the latter remain intact. To determine how iron stands to steel and how different amples of steel stand to each other, Mr. Thomson made an extended series of experiments, using a Thomson's tangent galvanometer to measure the electrical currents generated in the corrosion of iron and steel, both singly and in connection with each other, and when immersed in different fluids, viz.: sulphuric acid (one part to nine of water), caustic-potash solution (specific gravity, 1.311), and chloride-of-ammonium solution (specific gravity, 1.033), the latter representing electrically the ordinary concentrated water found in steam-boilers.

The details of the experiments are important, but I will give only the results obtained, viz.:

"When an iron rivet and a piece of the above-mentioned corroded steel furnace plate were placed in contact and immersed in the weak sulphuric-acid bath, at first the steel was electro-negative to the iron, but in a few moments it changed, and afterward the iron was electro-negative to the steel. When placed in the chloride-of-ammonium solution, at first the iron was strongly electro-positive to the steel, and afterward became *weakly* electro-negative. When placed in the caustic-potash solution, the steel was strongly electro-positive, but the current gradually became weaker and weaker until it practically ceased. A new steel rivet in an iron plate, a steel rivet closed by a machine and held until nearly cold, an iron rivet closed on a mild unworked steel plate, all reacted strongly among themselves. The iron when first brought into voltaic contact with the steel was strongly electro-positive to the steel, being presumably strongly acted upon by the solution, but after a few minutes almost ceased action or became reversed; and so far as the tests demonstrated as a whole, it was to the effect that it was quite as safe to bring iron and steel in close mechanical contact with each other as two different kinds of steel or two kinds of iron. Corrosion was developed in some degree in the contact of all different metals to each other."

It is cited that a number of torpedo boats of the French Navy, that had been constructed within ten years, and that had not made a thousand knots of sea service, were found to be so corroded at the water-line, though well painted from the first with anti-corrosive paints, they had to be condemned for service; while other boats of the same class that had never been in commission, but had been laid up under cover, had, as the report says, "eaten their own heads off by corrosion," and were condemned for the same cause. In these cases the corrosion had been in progress under the paint covering, and showed but little sign of its extent or progress, until the plates were so corroded in spots, many of them of large area, that the hammer used in testing the plates broke through the skin of the boats under the effect of blows that would not drive a nail into a pine block.

The use of anti-corrosive or anti-fouling paints, containing salts of any metal, is attended with the greatest danger to the coated structure. These pigments are extremely sensitive to the presence of saline elements in moisture, their action being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity.

Both mercury and copper salts are offenders in this way, but copper is by far the more objectionable, from the fact that the salts formed by the action of the sea-water upon the compounds used in the compositions are far more soluble than the corresponding salts of mercury, and are therefore liable to be present in much larger quantity, and so exert comparatively a much more injurious action on the plates.

As an illustration of this, two equal portions of sea-water were saturated, the one with copper chloride, the other with mercuric chloride, and into each a piece of steel planed upon one side and of about equal weight and size, was placed and left for four days. At the end of this period the two plates were removed, and after being cleaned and dried, were again weighed, when it was found that the one exposed to the copper-saturated sea-water had lost 22.2 per cent in weight, while the plate exposed to the mercurial solution had only lost 3.6 per cent, this being due to the much larger amount of the copper salt soluble in the sea-water.

On placing these plates in clean sea-water, corrosion went on in each case with extreme rapidity, and after being exposed for a month, they had both wasted to about the same extent; that is to say, when once deposited on the iron, mercury is practically as injurious as copper. See further data in Chapter XXXV.

In the year 1835, Mr. Peacock tried zinc plates on the bottom of H.M.S. *Medea*, and in 1867 Mr. T. B. Daft again brought the subject forward, Sir Nathaniel Barnabay, Mr. McIntyre, and others also suggesting various plans of attachment. In 1888 Mr. C. F. Henwood read a paper before the United Service Institute, strongly advocating zinc sheeting as attached by his system.

When the galvanic contact was small, then the sheeting had a certain life, but afforded *but little protection* to the iron, and gradually decayed away in a very uneven fashion; while in those cases where galvanic contact was successfully made, the ship on several occasions returned from her voyage minus a considerable portion of her sheeting.

Another drawback to the use of zinc sheathing is one which was found when it was used to coat wooden ships, and that is that sheet zinc, like every other metal, is by no means homogeneous, and that for this reason the action of the sea-water upon it, leaving out of consideration galvanic action, is very unevenly carried on, the sheeting showing a strong tendency to be eaten away in patches, while the metal itself undergoes some physical change and rapidly becomes brittle.

Attempts have been made to galvanize the iron before the building of the ship, but Mr. Mallett showed, in 1843, that this coating was useless when exposed to sea-water, as in from two to three months the whole of the zinc coating was converted into chloride and oxide; and when, therefore, galvanizing is used care must be taken to protect the thin coating of zinc. In any case the galvanizing must be done after the plates are riveted up, as any break in the surface would set up a rapid wasting away of the zinc, and the process could, therefore, be only used on small craft. Fresh water has less action upon the zinc than sea-water, and for this service galvanizing would be attended with some measure of success, the rapid wasting of the zinc in sea-water being due to the salts.

As has been before stated, if plates of iron or steel and one of copper be joined together or placed in communication and immersed in sea-water, acidulated solutions of water, or of mineral salts or oxides, the ferric body becomes electro-positive to the copper and is rapidly corroded. The corroded metal is always found in communication with the positive pole or current of electricity, the fluid soon becoming red from the rust formed.

In the corrosion of marine boilers, contact of different metals, strain, heat, and chemical action from the sea-water are all present and acting towards the same end. They are all of different potential and electro-positive, and none counteract each other, but all attack the boiler metals.

The voltage in this case is distinctly recognizable and evidently much different from the instances cited by Mr. Thompson of metals under strain only. In one reported case, it was one ohm, corrosion was marked and the current grew stronger as the corrosion increased.

Fresh water and solutions other than sea-water, also vapors, are corrosive agents to boilers, the corrosion of which is modified, corrected and rendered nil, by the use of electrogens, or heavy cast-zinc plates. In old boilers using fresh or salt water, the corrosion in progress is arrested by the use of the electrogens, so long as any appreciable amount of zinc is present. When the zinc is wasted away or removed, "bleeding" from the boilers at once begins, particularly in old boilers or in the tube settings.

In marine boilers, zinc 10″×6″×1″ to the amount of one square foot of surface to 50 square feet of heating surface is placed in clean, firm, metallic contact with the internal steam or water surfaces. Too much zinc is hardly possible and is better than too little. The amount of zinc can be reduced after a time to 75 or 100 square feet. The zinc must be placed in absolute contact with the bright metal at a number of points. Suspending the zinc in any form in trays or baskets will not prove effective. Zinc is slowly dissolved in hot water, and deposited as a sediment that can be removed by the blow-off, carrying with it any old scale or rust loosened by the galvanic action of the zinc. The boiler fluid contains a white flocculent precipitate of zinc (zinc oxide). If the water contains the sulphates or carbonates of lime or magnesia, silicates or other minerals, that form the usual hard, vitreous scale, the precipitated zinc oxide unites with them and holds them in solution until blown out.

Zinc causing old boilers to bleed, might be considered an injury instead of a blessing. It indicates that the boiler needs repairs to prevent future disasters.

The amount of zinc in boilers for land service using waters containing mineral substances, has not been so clearly ascertained as in the case of marine work; but the results in the latter case are a good basis to reckon from.

Any neutral salt in water which decreases its resistance, will enable it to act as the necessary liquid medium in a voltaic circuit.

The disintegration of the zinc in boilers forms the same oxide that is formed in the roasting furnace for pigments, i.e., 80.344 parts of zinc and 19.656 parts of oxygen. The hydrogen set free replaces that lost in the heating of the water, that in a measure is broken up at all heats below a low red heat, where complete dissociation of the hydrogen occurs. In both the steam and water, the flocculent particles of the zinc readily unite with any ammoniacal, carbonic, or sulphuric acids, saccharine, or other organic vapors or liquids present to form sulphates, carbonates of zinc, etc., that would act mechanically in the water to prevent deposit and cause corrosion.

Central-heating-system pipes develop a virulent corrosion. The reason for some of the cases is difficult to find. This corrosion has caused the abandonment of the pipes returning the condensed water to the boilers, and in some cases the failure of the whole system. The corrosion occurs in both the steam-pipes and water-return pipes, being more marked in the latter. In screwed-end pipes the corrosion first attacks the heel of the pipe threads as zones of disintegration and extends until the whole pipe is affected, though no corrosion except at the joints may be noticed.

In the steam-pipes corrosion takes the form of pin-holing or pitting, from the inside at any part of the pipe and does not develop into a general corrosion of the surface as in the case of the hot-water return pipes. Whenever a blow-out or pin-hole from corrosion occurs in the steam pipe, a closing down of the metal around the hole by a peen hammer stops the leak, which seldom reopens. Peening the metal has made it more dense and less liable to corrode.

Cast-iron steam-pipes are less affected than wrought-iron pipes, but the joints draw badly, owing to the temperature changes that cause a leakage that frequent caulking only momentarily corrects. Cement joints are unreliable under high temperatures, while rust joints owing to their own corrosion burst the sockets of the pipes.

In central-heating systems, the losses from leakage and condensation amount to from 30 to 35 per cent yearly, aside from the loss of the return water; while the corrosion losses are about 10 per cent of the cost of the pipe lines.

Particles of dirt, cinder in excess, unabsorbed carbon or manga-

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"Use of Zinc in the Steamship Hindostan," *Engineering*, August 7, 1878.

"The Corrosion of Steamship Boilers." *The Practical Engineer*, Vol. X, September 28, 1894.

"The Corrosion of Boilers." *The Engineer* (London), Vol. LXXVIII, 1894, p. 208–281.

nese and impurities in the metal have all been blamed for the erratic disintegration of the pipes, which continues after many of the above causes have been removed.

In all of these pipes a low density, open-grained filament-formed iron, cinder in excess, heat, motion of vapor and water under pressure are all present, and no protective covering of moment. The hot water is more effective than steam in keeping the pipes clean and bright, ready for corrosive influences.

The disturbance of water by high heat in being partially dissociated has been already explained in this chapter. The action of zinc on electrogens, in the case of marine boilers and sea-water corrosion, is always favorable for the preservation of the metal. The use of zinc to prevent corrosion in steam-pipes, radiator and heating lines, could be hardly less favorable.

M. Loudin's (*Comptes Rendus*) experiments on the corrosion of iron immersed in water usually found in steam-boilers, was: That with both ordinary and distilled water, the temperature had a very important influence, viz.:

"At 68° F. the quantities of oxygen absorbed per square foot of iron surface per hour, when immersed in distilled water was 0.258 grain and in calcareous water 0.330 grain. At 212° F. the quantities rose to 2.364 and 2.579 grains. The immersion of iron in water at all ordinary temperatures was attended by the evolution of hydrogen, the action being the least in distilled water. At a temperature of 260° F., the decomposition of distilled water was equal to the absorption of 0.01 grain per square foot of ferric surface per hour, and for calcareous water, 0.0129 grain. For water containing one-fifth part of crystallized chloride of magnesium, corrosion was 0.0182 grain per square foot, and for water saturated with chloride of sodium, 0.05 grain; for sea-water of usual density, 0.067 grain, all per square foot of iron surface per hour immersion."

Corrosion Increased by Stress.

The tendency of iron to change its physical properties by a change in the condition under which it may be placed in ordinary structural work is strikingly shown by the following instance taken from *Engineering*, April 27, 1894, and reported by Mr. Oswald Brown, M.I.C.E., of 32 Victoria Street, Westminster.

"The cut (Fig. 51) shows portions of the bar dark and corroded, while the intermediate layers have remained bright. The bands of rust extend over both ends of the bar, giving it the appearance of being built up of layers of two different metals. The bar, which is of the best Yorkshire iron, gave under test the following results:

"Tensile strength, 54,230 pounds per square inch; elongation on 8 inches, 28.4 per cent; contraction of area, 49.6 per cent. No traces of lamination were shown during the test, but *some months after*, the bar was found in the condition illustrated, which shows that it consists of layers of different chemical composition, those which have rusted being electro-positive to the other portions of the bar."

Fig. 51.—Effect of strain on the corrosion of iron.

Iron rivets and iron plates in some cases show the rivets corroded and the plates unaffected, and sometimes the contrary, and so with steel rivets and steel plates; also iron rivets in steel plates or steel rivets in iron plates all show the most erratic evidences as regards corrosion, in many cases without reference to the character of the water used in the boiler or to the external conditions. As a rule, all analyses of the plates, rivets, and other material used in boiler work are made from samples as they come from the manufacturer's hands, and before being worked. Hence, when corrosion of either plate or rivet has attracted attention, it is seldom possible to get a sample of that particular make and lot of rivets to analyze to show what physical changes were developed by the processes of heating, closing the rivet, cold-hammering the head, chipping, caulking, etc. These processes, also punching instead of drilling the holes, develop corrosion, that takes the form of pitting around the rivets and furrowing on the sheet joints.

Mr. Thomas Andrews, F.R.S., reporting to the British Institution of Civil Engineers, states his conclusions *On the Effect of Stress on the Corrosion of Metals.** In brief they are:

"That wrought iron and various steels, when exposed separately, without liability to galvanic action other than local, under the action of sea-water for long periods, showed a greater corrosion on the part of all the steels than the wrought iron; the advantage in favor of the iron compared with the steels amounting to 25 per cent and upward. It was also noticed that corrosion was increased in the steels in proportion as the percentage of combined carbon was greater.

"It was found that the galvanic action between wrought iron and steels induced a largely increased corrosion in both metals. It was also found that the upper and lower portions of a metal structure, or vessel, although composed throughout of the same metal, were exposed to electrolytic disintegration from the galvanic action set up by solutions of different salinity on the metal; conditions found almost constant in tidal streams, brought about by the gradual rise and inflow of salt water and the outward flow of fresh water; and there are strong evidences to show that magnetic influence tends to increase the corrosion of metals.

"When, however, the strained metal is in galvanic circuit or combination with the unstrained metal in any solution, an increased total corrosion ensues from the galvanic action, which research has shown to arise consequent on the different potential between the two.

"It was demonstrated that *stress of any kind* considerably alters the physical properties of both iron and steel, by increasing their rigidity and rendering the metals harder, also greatly reducing their properties of elongation or ductility. It requires a higher tonnage to break a strained than an unstrained bar of the same metal. A tensile stress applied to a wrought-iron shaft, that produces an elongation of only 2 per cent, increases the tensile resistance of the metal 2.66 per cent.

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* Proceedings of the Institution of Civil Engineers (English), Vol. CXVIII, 1893–94, Part IV, p. 356.

The Practical Engineer (London), Vol. X, No. 398, October 12, 1894.

Iron Age, Vol. No. 17, October 25, 1894.

Minutes of Proceedings Institute Civil Engineers, Vol. LXXXVII, p. 340, and Vol. XCIV, p. 180; also Vol. CV, p. 161.

"From the observations it was manifest that the stresses applied to metals altered their structure, rendered them harder in nature, and more liable while in their strained condition to be acted upon by sea-water, or other waters, than in their ordinary normal or softer condition. The experiments, however, indicate that an *increased total corrosion,* in excess of the normal corrosibility of the metal, occurs in a metallic structure, from the action of the *local* galvanic currents which are shown to be induced between strained and unstrained portions of the same piece of iron or steel forging, bar, or plate. Hence a strain occurring in a metallic structure tends, *owing to the local* galvanic action thus set up, to increase any corrosive forces which may be deteriorating the metal of which it is composed."

The details of the experiments are: Pieces of iron and mild steel of known character were submitted to tension, torsion, and flexure strains, to ascertain the changes made in the metal, and if corrosive effects were in any manner due to stress. For tension, a bar was strained in a testing machine until an elongation was produced of 23 per cent in three inches, and at the point of reduced area the bar was cut in two.

The halves were then turned down at the shackle or vise end, where they had been subjected to little or no stress, until they had an area equal to the end half at the point where contraction of area had occurred, both pieces being finished exactly alike and each piece represented a section of strained and unstrained metal. They were then placed at the same depth in a saturated solution of common salt to approximate the action of sea-water on metal, the immersed ends representing strained and unstrained metal. An electrical contact made between the two pieces of metal, through the medium of a delicate galvanometer (Thomson's), the difference in potential or corrosibility could be observed. It was found that in each case a sensible current was set up between the two halves of the specimen; the strained portion was in every case found to be the electro-positive element of the pair, corresponding to the zinc in a galvanic couple, indicating clearly that the strained metal was acted upon more rapidly by the solution, and more easily corroded than the unstrained metal.

The test made with specimens after being submitted to torsional stress, representing a bar that had been twisted through an angle equal to half a revolution, and prepared similar to those in the tensile test, showed results identical with the tensile strains. In every instance the strained metal was the electro-positive element, and was corroded more rapidly by the sea-water.

This conclusion was further supported by tests made with iron and steel plates, when a flat piece was compared with one bent into an U or semi-circular trough; the bent plate in each case proving to be the one most easily acted upon by the solution.

The experiments throw an interesting light on a subject which has hardly received the attention it deserves, and helps to explain some of the peculiarities in connection with the wasting of certain structures that have been involved in considerable mystery. The metals operated upon by Mr. Andrews were large, rolled wrought-iron bars and hammered wrought-iron shafts; Bessemer steel and Siemens steel forged shafts, also large bars of soft and hard Bessemer and Siemens steel; soft and hard cast steel, and steels made from each of the metals aluminum, nickel, silicon, and copper. Experiments were also made on *rolled* plates of wrought iron, soft Bessemer and soft and hard Siemens steel and soft cast iron. The chemical compositions and general physical properties, etc., of all the metals are given and tabulated. All the metals experimented upon were perfectly bright.

General results: The average electromotive force obtained between strained and unstrained portions of the same metal were, viz.:

Wrought-iron forged shafts	0.016	volts.
Soft Bessemer steel forged	0.019	“
Hard “ “ “	0.006	“
Soft cast steel	0.003	“
Hard “ “	0.003	“
Silicon steel	0.004	“
Aluminum steel	0.004	“
Nickel steel	0.003	“
Rolled wrought-iron bars	0.002	“
Soft Siemens steel	0.005	“
Hard “ “	0.005	“
Copper steel	0.006	“
Chromium steel	0.001	“
Bessemer steel hammered forgings	0.011	“
Siemens steel “ “	0.006	“

With cold-drawn small steel rods in galvanic circuit with copper rods, similar results were noted, the electromotive force between strained and unstrained aluminum steel being 0.022 volts, and strained and unstrained cast steel being 0.023 volts.

In all these tests the *strained* metal was the electro-positive. In the torsional tests the electromotive force was notably higher than in the tensile, also in the flexure, tests.

These electric measurements ought, perhaps, to be regarded as tentative indications, establishing a general principle, rather than as an absolute measurement for the purpose of accurate comparison of the behavior of the various metals. The chemical analysis of all the metals was made prior to straining them. These experiments extended from a few seconds to over ten days, in which it was observed that the difference in the electromotive force between strained and unstrained metal steadily declined from the initial amount, but was in no case extinguished.

Corrosion, or the oxidation of substances by chemical action is always accompanied by electrical energy, that may be of more or less intensity, or electromotive force according to the substance consumed.

Chemical action is probably due to the unbalanced attraction among the various molecules of matter lying in juxtaposition, the rearrangement of which caused by strain or a change in the thermal or electrical conditions of one atom changes them all. It is known that a change in either the thermal or electrical conditions develops corrosion in certain circumstances but does not in many other cases of apparently the same nature. The amount of electromotive force developed in the oxidation of a few substances is indicated in the following instances: *

Substances.	Heat of Oxidation of Equivalent. Calories. B. T. Units.	E.M.F. Relative to Oxygen.	E.M.F. Relative to Zinc.
Carbon	2,000 = 7,938	0.09	−1.74
Silver	9,000 = 31,742	0.39	−1.44
Copper	18,760 = 74,057	0.80	−1.08
Lead	25,100 = 99,616	1.12	−0.71
Iron	34,120 = 135,415	1.55	−0.28
Zinc	42,700 = 169,074	1.83	0.00
Peroxide of lead	12,500 = 48,022	0.52	−2.35

The corrosion of ferric bodies results from the decomposition of water or air by electrical energy.

As detailed in Chapter III, atmospheric moisture in the presence of iron at a temperature of 900° F. releases oxygen and forms the

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* Thompson's Electricity and Magnetism.

black magnetic or stable oxide of iron, that in manufactured articles is represented by the Bower-Barff products.

Every pound of iron oxide represents the energy of 1.668 pound of coal required for its formation. This rust requires .3375 pound of water to furnish the necessary oxygen. A pound of iron oxide represents the corrosion of 13.13 square feet of metallic iron $\frac{1}{1000}$ inch in thickness and has developed 163,233 B. T. Units (.0641 H.P.), or equal to an electromotive force of 1.55, to neutralize which would require the oxidation of .847 pound of zinc.

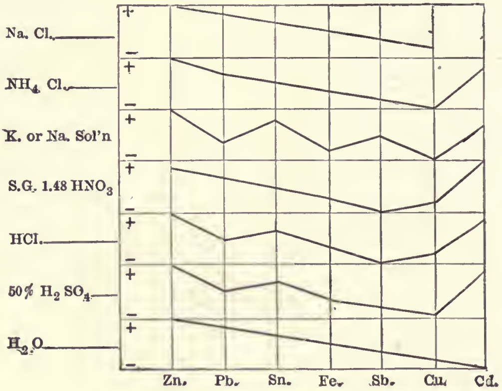

FIG. 52.—Diagram of the corrosibility of metals.

In all of these oxidations the thermal manifestations are subordinate, and, with the electrical energy being of low potential, when they extend over any considerable period, are unrecognized or difficult to determine.

The affinity of oxygen for hydrogen represents an electromotive force of 1.47 volt. The decomposition of water acidulated by sulphuric acid yields at the cathode 11.12 parts of hydrogen and at the anode 88.18 parts of oxygen; about 1 per cent of ozone being formed from the oxygen.

The decomposition of 1 pound of zinc for the protection from corrosion of marine boilers or other like ferric bodies evolves 9840 cubic inches of hydrogen, equal to 5.694 cubic feet, that weighs 210.29 grains, or .3329 pound.

The late Henry Morton, Ph.D.,* stated that a pound of zinc consumed in the following-named batteries develops:

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* "The Maximum Possible Efficiency of Galvanic Batteries." *Cassier's Magazine*, June, 1895, p. 130.

	B. T. Units.	Horse-power.
Smee's battery	900	0.35
Daniels's (sulphate of copper) battery	1419	0.55
Grove's or Bunsen's (nitric acid) "	2722.4	1.06
Peggendorf's (chromic acid) "	2827.5	1.14
Sulphuric acid (1 in 9 parts of water)	3006	1.17

All losses from resistance being excluded.

A series of experiments covering several years, upon the corrosibility of metals, has been made at the University of Wisconsin, under the supervision of Prof. Dugald C. Jackson.

Prof. Jackson, in the discussion of paper No. 901, "Protection of Ferric Structures,"* referred to the results of his experiments, from which I briefly quote: "When a piece of iron or steel is placed in a testing machine and its electrical condition is followed up during the straining test, *its corrosibility appears to increase practically in proportion with the strain,* so that a diagram plotted with stress along one coordinate and corrosibility along the other appears to be of almost exactly similar character to a diagram plotted with stress and strain along the two axes of coordinates.

"Two illustrations of these diagrams are presented, Figs. 53 and 54, from test pieces of wrought iron

"In the case of cast iron Fig. 55 shows the stress-corrosibility diagrams for two specimens in tension. A comparison of these diagrams with those for wrought iron in tension, illustrated in Figs. 53 and 54, shows the marked difference between the two metals. Fig. 56 shows a stress-corrosibility diagram for cast iron in compression. The exact forms of the diagrams taken from cast iron depend in some degree on the physical character of the specimens, but the diagrams shown are typical ones. The effect of strain is small in the case of cast iron.

"The corrosibility of the specimens was measured by determining the electromotive forces of the test pieces toward a standard electrode in a normal solution.

"The results of the tests show that in bridge members and similar pieces that have been worked, the metal appears to be *easily affected* by corrosion, this corrosion being properly characterized as

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* Transactions American Society Mechanical Engineers, Vol. XXII, Paper No. 901, May, 1901.

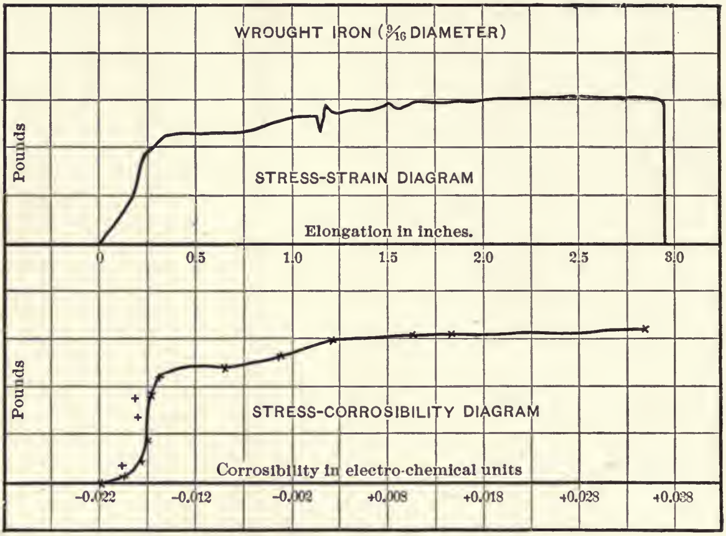

Fig. 53.—Stress-strain and stress corrosibility of wrought iron.

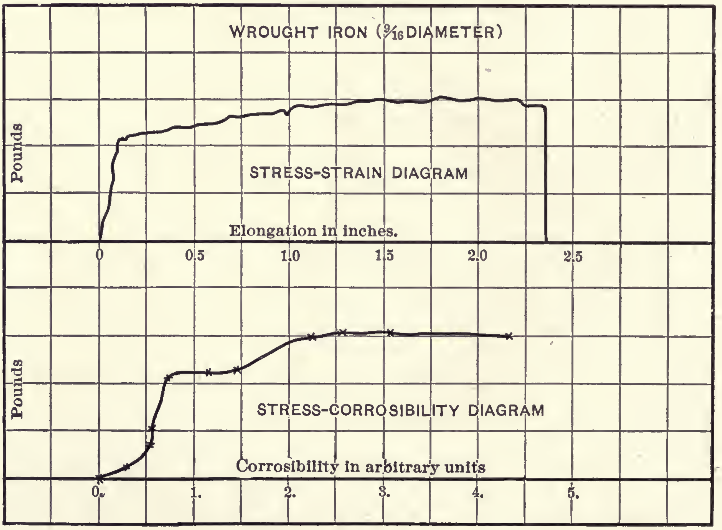

Fig. 54.—Comparison of stress-strain and stress-corrosibility diagrams, wrought iron.

caused by electrolysis; that is, the strained metal is really eaten away and the unstrained metal is not.

"The experiments give a satisfactory explanation of much of the so-called grooving in boilers and corrosion of a similar character. Here the strained metal of a punched boiler plate that is not completely covered by a rivet-head becomes eaten away. Or perhaps a plate becomes strained at a joint by temperature stresses and the strained streak is corroded. In each case *the strained metal is of greater corrosibility,* and it acts as one of the plates of an electric battery in which the other plate of the battery is the unstrained metal of the boiler shell, and the electrolyte is the water within the boiler. The strained metal is the electrode which corresponds to the zinc of the ordinary voltaic cell, and it is eaten away.

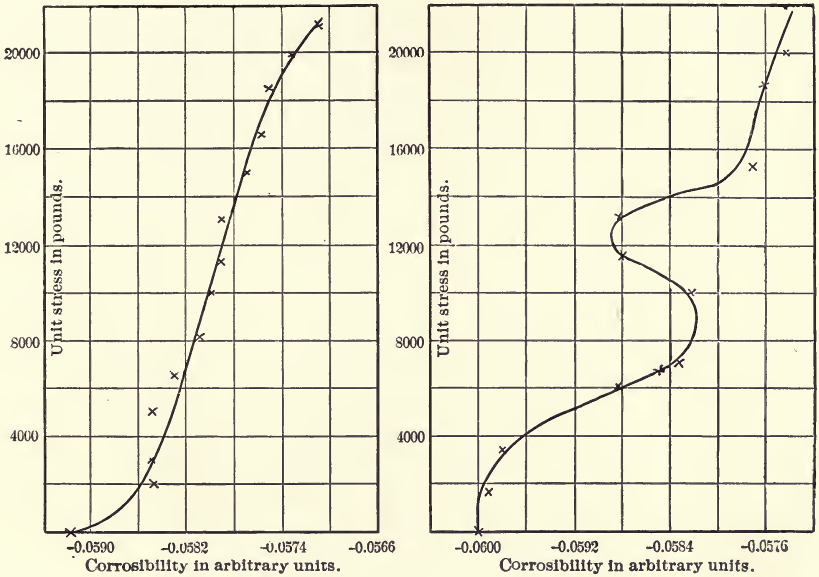

FIG. 55.—Stress-corrosibility diagrams for cast iron.

"Another illustration of corrosion of this character is the so-called (by bridge engineers) Cooper's lines, which are often evidenced in the corrosion of bridge members. These are lines of electrolytic corrosion in strained parts. The most seriously strained parts, or parts that have become hardened in working, are eaten away by voltaic action, which goes on at their expense, and the less strained

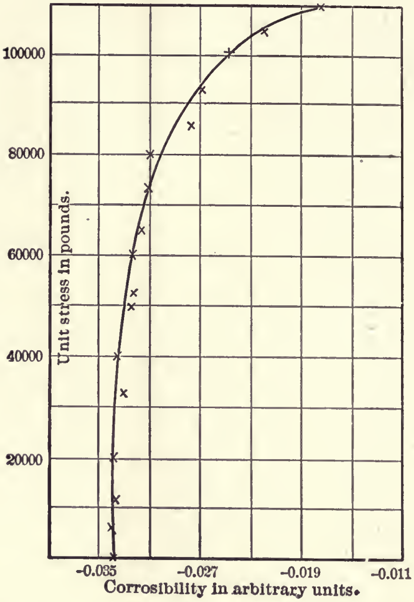

Fig. 56.—Stress-corrosibility diagram of cast iron in compression.

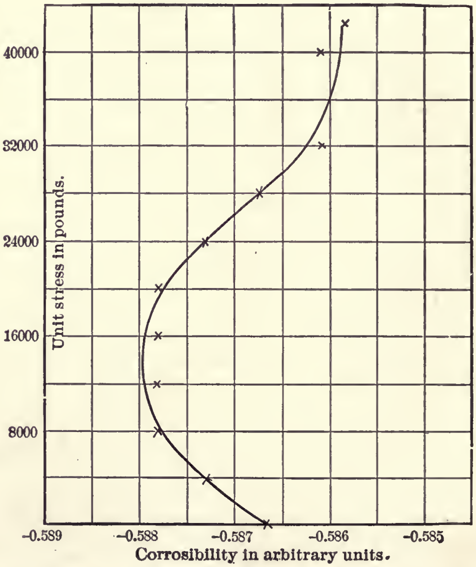

Fig. 57.—Stress-corrosibility diagram of hard-drawn copper wire.

parts are less rapidly corroded, thus leaving the appearance of lines of corrosion.

" It is also true that metals which do not change their physical characteristics when strained, apparently do not materially change in corrosibility as the result of strain. Thus if lead is stretched, its corrosibility does not appreciably increase. The same is true to a certain degree of brass and copper. Fig. 54 represents a stress-corrosibility diagram for hard-drawn copper. The same is true also, to a limited degree, of very soft iron, but as even the softest iron does harden sowewhat when strained, its corrosibility is somewhat affected by strain."

An experimental study of the corrosion of iron and steel under different conditions has been made by Mr. Carl Hambuchen, B.Sc.* These experiments were conducted on the lines of those of Mr. Thomas Andrews, F.R.S., hereinbefore given, "on the effect of strain on the corrosibility of metal."

Hambuchen's apparatus and method of testing, and the checks and precautions against errors, especially in obtaining the value of the electromotive force, were superior to those heretofore employed by experimenters, and the results are more in accordance with the practical experience of the present day.

A hindrance to experimental investigation of the corrosion of metal is the length of time required to produce measurable results. Hambuchen took advantage of the fact that corrosion being developed by an electric current flowing from the ferric body to the electrolyte, the rate of corrosion could be greatly increased by causing a current generated externally to flow from the metal as an anode, thus causing the corrosion to occur under what may be termed exaggerated or intense conditions, the metal being corroded as much in a few hours as it would be in as many years by exposure to the weather; the resultants being practically the same as the effects produced by ordinary corrosion.

The losses in weight from corrosion in different irons, steels, and other metals, under strain, from *nil* to breakage, are tabulated, also the loss in weight of metal per ampere hour, and the electromotive force developed at various points of the strain.

Normal solutions of ammonium chloride, ammonium sulphate,

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* Excerpts from Bulletin of the University of Wisconsin, No. 2, Engineering Series. Vol. II, No. 8, July, 1900. Illustrated.

potassium nitrate, sulphate and chlorides of nitre, were used for the electrolyte. The experiments determined that the loss in weight of the metal in the different solutions was practically the same, and that whether the salts were sulphates, nitrates, or chlorides did not materially affect the rate of corrosion. The ampere hours varied from 11 to 13.6 and the exposures from 19.5 to 24.25 hours.

Interesting facts were developed showing the variable nature of "pitting" in mild steel exposed to different solutions. Figs. 58 and 61 show a round pitting as the result of the ammonium chloride; an elongated pitting results from the ammonium sulphate, and a more uniform corrosion from a potassium-nitrate solution. In the cast-iron specimens, Fig. 59, the corrosion consisted of a soft carbonaceous material, which generally adhered very firmly to the surface of the iron. In case the current density was carried beyond 0.025 amperes per square inch, this soft material would separate from the iron after attaining a certain thickness. The formation of this layer must offer some resistance to the flow of the current, and therefore protects it to a certain degree. Or, in other words, a given potential difference between an iron pipe and a railway track would cause less flow if the pipe thus coated were cast iron, than if it were wrought iron, which would quickly reveal its weakness by the different character of the corroded coating. But with a given amount of current flowing from normal cast iron and wrought iron, the corrosion is nearly equal in amount in the two.

It was noticed in the case of the cast-iron anodes that there was a liberation of gas during the process of corrosion. That this was not due to the flow of the current was shown by interrupting the current, the liberation of the gas continuing for some time after. The nature of the gas was not determined, nor of what the action consisted.

If the current density was not excessive, the iron did not undergo any material change in appearance, even though subjected to the action of the current for a long time. But although the general form and outward appearance of the cast iron remained the same, the fact that its structure had been materially altered was shown by cutting it. The cast iron was found to be softened to a certain depth, the material removed having the appearance of fine iron filings and graphite, making the loss to the iron equal to 1.17 grains per ampere hour for 10.72 square inches of exposed area. This coating if allowed to stand until dry became much harder and offered some resistance to cutting; but the iron had lost its original strength.

The effect of the presence of mill-scale on the rapidity of corrosion is shown by Figs. 58–61 and 65 in comparison with the polished plates of the same metal.

Changing the crystalline structure of steel by annealing, hardening, and burning, causes the amount of corrosion to vary, as is noted in the tables on pages 363–364. The amount of corrosion per ampere hour of the hardened steel is considerably less than that of the annealed or burned steel.

This is an apparent discrepancy with other data and observations in regard to strained metal being the most subject to corrosion. Hardened steel, being necessarily under a highly strained condition, should have shown greater corrosibility than the annealed or burned specimens. That it did not is owing to the fact that the high tension between the particles held them in place until they were severally corroded entirely away. In the burned or annealed steel the particles, when only partially corroded, were loosened in their bond to each other, and cast from the mass before being entirely corroded. The pitting of the annealed steel, Fig. 66, the composition of which is similar to that of sheet iron, Fig. 72, shows a greater corrosibility than the hardened steel, due to the above reason.

The small percentage of carbon and other impurities in the steel would not account for the corrugations in the burned and hardened steel, shown by the figures. It would be unreasonable to suppose that the impurities or carbon could be regularly distributed as indicated by the corrugations; they must be due to lines of strain in the metal that corrosion developed.

The metals that are electro-positive to iron and steel are magnesium, aluminum, zinc, and cadmium; while lead, antimony, tin, copper, silver, carbon, manganese, and some of the metallic oxides, are electro-negative to ferric bodies.

Test plates of clean, bright wrought iron, cast iron, and steel were drilled and the several holes plugged with one of the above metals. The plates were then placed in sand saturated with ammonium chloride and other corrosive solutions, and after a short exposure were examined; all the plates in which the electro-positive metal plugs were placed were found clean and bright, while the plugs were more or less corroded. In the other set of plates the surfaces were corroded while the plugs were not affected. In the plates fitted with the zinc and other electro-positive metals, the current flowed from the solution to the plates and corrosion did not take place.

In the plates with the lead, carbon, and other electro-negative substances, the current flowed from the plates to the solution and the plates were corroded.

The conditions of electrolytic corrosion apply to most of the metallic oxides as well as to the metals, and are developed in both: 1. When two or more conducting substances are in contact with an electrolyte. 2. Whenever there is any difference of electrical potential between such bodies. 3. When a suitable connection between the conducting substances furnishes a path for the flow of the current.

All of these conditions are present in the decay of paint coatings as well as the corrosion of iron and steel. The electrolyte consists of moisture in any form, and may be acidulated, saline, or fresh.

Iron and steel rea never pure or homogeneous; they contain upon their surfaces many substances, such as carbon, graphite, mill-scale, and particles of metal and oxides. The body of the metal may be formed from scrap iron of different natures, and the heat of fusion seldom renders the mass homogeneous.

In cast iron and steel, in their many processes of manufacture, there are many irregular zones of density and purity each of which has its own potential. Between all of these differently charged bodies a current of electricity is set up, the circuit being completed through the electrolyte.

This electric current flowing from the metal to the electrolyte will cause corrosion of the metal, which may be general over the whole surface of it, or be localized in spots, according to its composition, which is affected by local disturbances, such as welds, strains, annealing, burning, and hardening, or the presence of foreign substances. Some peculiar cases of corrosion can be explained by ascertaining if the metal has been subjected to some of these influences, that otherwise would be classed as mysterious.

Mr. Hambuchen, in order to draw a comparison between electrolytic corrosion and ordinary corrosion, immersed specimens similar to those exposed to electrolytic action in a tank containing a normal solution of ammonium chloride, and left them undisturbed for four months. The results obtained showed that the amount and character of corrosion depend upon the quality of the metal, and confirmed the conclusion derived from electrolytic corrosion. The time of exposure of these specimens was, however, too short to develop any marked pittings or other corrosive effects shown so plainly in the electrolytic samples.

Some of the conclusions given by Mr. Hambuchen as the result of his tests are:

That electrolytic corrosion produced by the flow of a current of moderate density from an external source, produces results on the metal which are similar to those produced by corrosion under ordinary conditions.

In many if not all cases the character and rapidity of ordinary corrosion of iron and steel depend upon their physical and chemical properties, and the galvanic action due to differences in potential between different parts of the metal.

The application of stress to metals causes an increase in chemical activity, this increase being especially marked after the elastic limit is reached.

It is possible to plot a curve showing the relation of electromotive force to strain, which is similar to that of stress to strain.

There is a definite relation between the electrical potential of any metal toward an electrolyte and the amount of energy stored up in the metal through the application of stress. It is evident that the protection of ferric structures from corrosion requires their removal from electrolytic influences.

The several specimens subjected to different conditions of corrosion were all taken from the same bar or sheet to facilitate comparison.

The following tables are means of a few of the separate results given by Mr. Hambuchen:

Table showing the loss in weight of iron and steel used as anodes, immersed in a solution of ammonium chloride and exposed to the action of an electric current of varying densities and time.

Material and Condition of Surface.	Area in Square Inches.	Total Loss in Weight. Grams.	Weight Lost per Ampere Hour. Grams.	Ampere Hours.	Exposure Hours.
Annealed steel, polished.	10.	15.9	1.1683	13.6	23¾
" " with scale.	10.523	15.33	1.1163	13.3	19½
Hardened steel, polished.	10.	14.633	1.077	13.6	23¾
" " with scale.	10.48	14.407	1.059	13.3	19.5
Steel burned, not hardened or polished.	10.	15.666	1.1526	13.6	23¾
Steel burned, not hardened with scale	10.3	15.515	1.1575	13.3	19½
Steel burned, hardened, and polished	10.555	12.875	1.1475	11.2	24¼
Cast iron, polished.	10.073	12.273	1.0983	11.2	24¼
" " scale partly removed.	10.693	9.996	0.7506	13.3	19½
Sheet iron, polished.	10.373	13.87	1.184	11.2	24¼
" " scale partly removed. . . .	10.263	14.63	1.084	13.3	19½

It will be noticed that the amount of corrosion for all of the specimens is greater per ampere hour than the theoretical amount given by Faraday's law (1.0448 grains per square foot of surface per ampere hour), cast iron with the scale partly removed being an exception.

Table showing the loss in weight of iron and steel exposed to corrosion by immersion for 4 months in a solution of ammonium chloride.

Metal and Condition.	Area in Square Inches.	Total Loss in Weight. Grams.	Loss in Weight per Square Inch. Grams.
Sheet iron, surface polished	10.437	0.733	0.066
" " scale partly removed	10.30	1.473	0.142
" " with scale	10.556	1.793	1.698
Cast iron, surface polished	13.596	1.083	0.0793
" " scale partly removed	14.16	1.663	0.117
" " with scale	14.117	1.663	0.1174
Annealed steel, surface polished	10.37	0.733	0.0708
" " scale partly removed	10.603	1.08	0.102
" " with scale	10.336	2.00	0.193
Hardened steel, with scale	10.57	1.063	0.9985
Steel with scale, burned not hardened	10.255	3.70	0.3613

FIG. 58.—Mild steel (ammonium-chloride solution). Magnified $2\frac{1}{8}$ diameters.

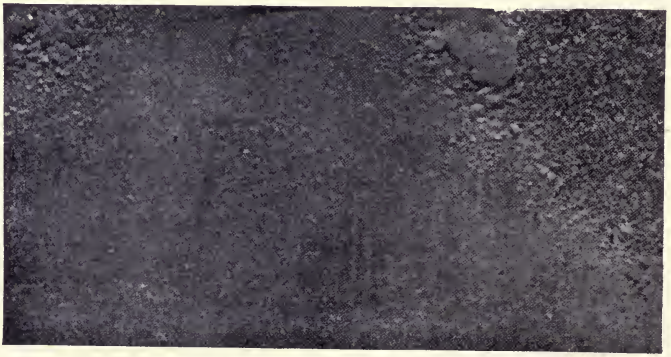

FIG. 59.—Cast iron (polished). Magnified $2\frac{1}{8}$ diameters.

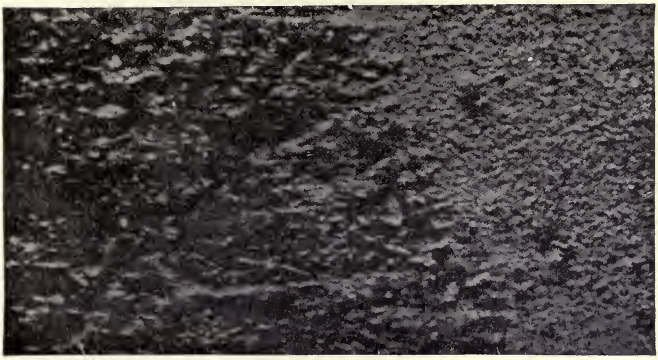

FIG. 60.—Cast iron (with scale). Magnified $2\frac{1}{8}$ diameters.

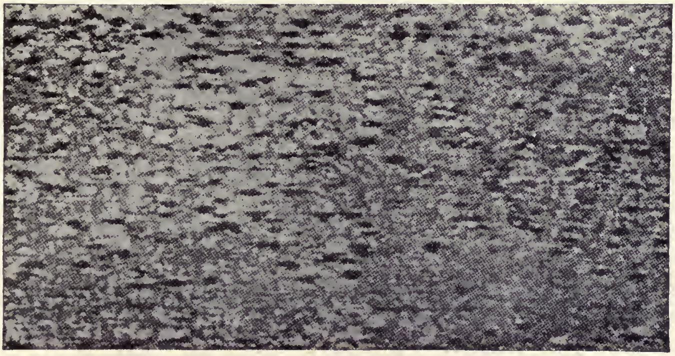

FIG. 61.—Mild steel (ammonium-chloride solution). Magnified $2\frac{1}{8}$ diameters.

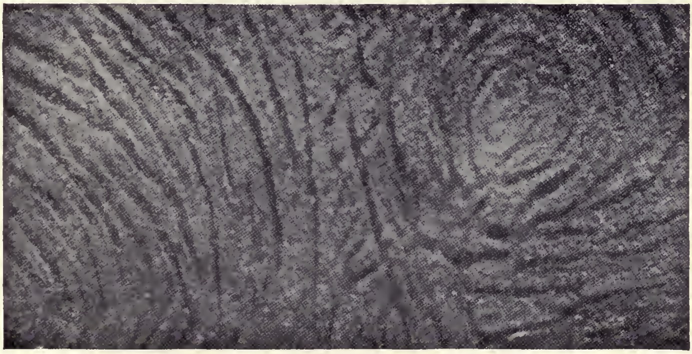

FIG. 62.—Burned and hardened steel. Magnified $2\frac{1}{8}$ diameters.

FIG. 63.—Burned steel not hardened (with scale). Magnified $2\frac{1}{8}$ diameters.

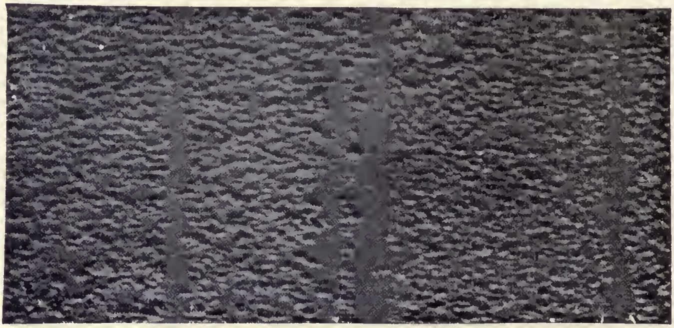

FIG. 64.—Annealed steel (polished). Magnified $2\frac{1}{8}$ diameters.

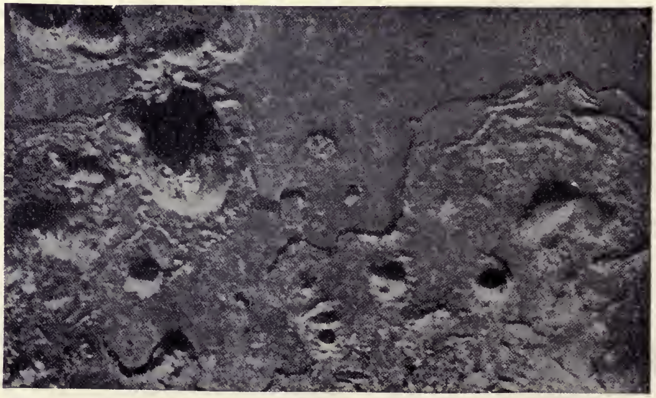

FIG. 65.—Annealed steel (with scale). Magnified $2\frac{1}{8}$ diameters.

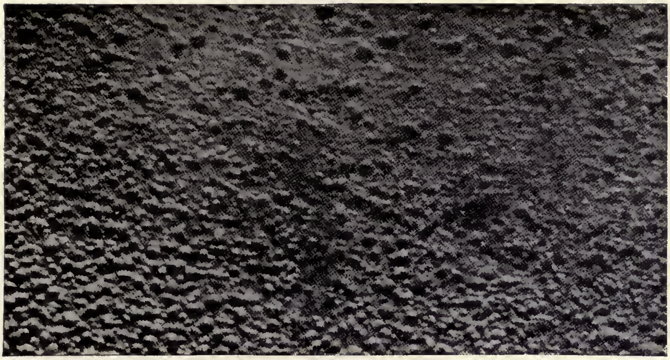

Fig. 66.—Steel burned but not hardened (polished). Magnified 2⅛ diameters.

Fig. 67.—Hardened steel (polished). Magnified 2⅛ diameters

Fig. 68.—Hardened steel (with scale). Magnified 2⅛ diameters.

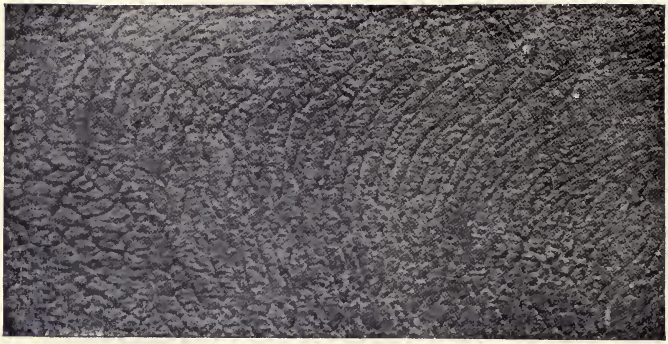

Fig. 69.—Steel burned and hardened (polished). Magnified 2⅛ diameters.

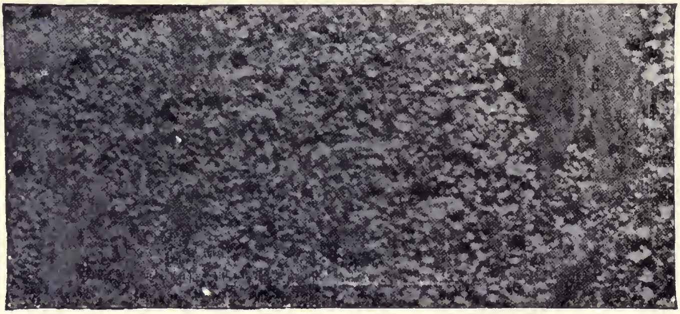

Fig. 70.—Sheet iron (polished). Magnified 2⅛ diameters.

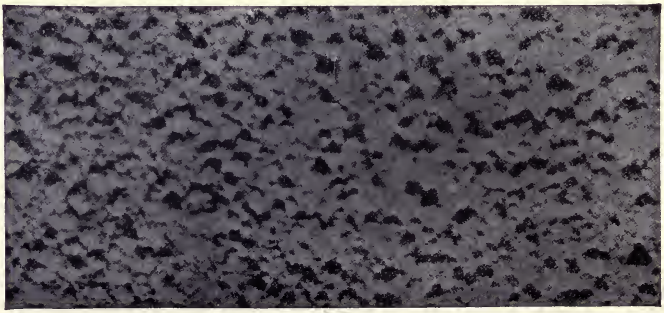

Fig. 71.—Sheet iron. Magnified 2⅛ diameters.

FIG. 72.—Sheet iron (with scale). Magnified $2\frac{1}{8}$ diameters

CHAPTER XXXIV.

ELECTROLYSIS OF UNDERGROUND METAL.

PROF. EDWIN J. HOUSTON defines electrolysis as chemical decomposition effected by means of an electric current; that is, the source of electrolytic corrosion lies in the release of an atom of oxygen from any moisture and its instantaneous combination with any iron it can seize upon."

Prof. D. C. Jackson (University of Wisconsin) defines its action: "In an electrolytic cell with iron electrodes, having any salt or salts of alkaline metals or earths in solution in the electrolyte, the salts are decomposed, their acid radicals attacking the anode, forming an iron salt.

A proof of this theory is found in the storage battery, in the charging of which a large current is discharged from a lead plate into an electrolyte consisting of dilute sulphuric acid. In a storage battery the oxidation of both plates takes place but the red oxide of lead formed is very different in character from the corrosive effects of an electric current on an underground lead-pipe."

* "There is nothing mysterious about the corrosion of metals by electrical currents. Its action is precisely similar to that employed by electro-platers in their art. Two plates of metal placed in any material, whether damp earth or the solution vat of an electroplating apparatus, a current of electrical energy will be instituted from one plate to another and the plate or object from which the current flows will be corroded. The current will make its own selection as to its course and the body to be attacked. In the case of metals buried in earth or water, the electrolytic action is out of sight and probably out of mind, but none the less present and uncontrollable; while in the plating bath it is in sight and controllable more or less, at the will of the attendant. In the case of high voltage and large ampere currents returning to their source of generation, it is one of the laws of electricity that where a current has two paths to

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* "Electrolysis," *Engineering Record*, August 21, 1899.

reach this point (and all electrical currents have two paths), the current will divide and return to its source in the direct ratio of their conducting capacity, whatever these conductors may be. Even with large and well-bonded metal return conductors buried in the earth or in conduits, some of the current will invariably pass by way of the earth and reach any outlying metallic bodies. The low voltage of .001 to .01 and the amount of amperes will determine the rate of corrosive effect in all metal in their course."

The advent of the steel building almost simultaneous with the introduction of the dynamo, has added not another form of corrosion, but a new field for its development and a new danger.

The principal part of the metal in steel frame structures is so embedded in masonry as to render inspection of its condition almost impossible. The pipe systems are more accessible, but are nevertheless at all times a ready prey for electrolysis.

Three hundred horse-power of electrical energy are not uncommon installations for light and power in one building. Whether led in from the outside, or generated in the building does not change the effect, which is to disturb the normal electrical conditions of all metals in the immediate neighborhood and in many cases those far distant.

In the return of this energy from its work to its generating source, if the pathway is not made perfectly free by the use of a conductor of adequate size, or if it be of such a length as to render a shorter and better circuit through other objects possible, then the current will jump the line wholly or in part. On the new route, wherever it leaves the metal, another jump will occur, and the metal will be corroded at that place, and not where the energy entered. There is always moisture enough in any building to afford adequate oxygen for the corrosion.

In the steel frame work of the building, the electrolysis will be at the foot of the columns nearest to the least resisting pathway of the current, generally at a point impossible to locate or inspect, and with moisture in excess to make a good cross-cut and dangerous circuit.

In the iron pipes there usually will be a jump at every joint, if it is made by the hemp gasket and lead, or by a hydraulic cement method. The screwed ends of wrought-iron gas and water-pipes also are affected by the difference in resistance between the two natures of the same metal, and sheet iron used for shims between columns and girders have been found to be the cause of a jump corrosion, particularly if aided by the presence of damp dirt or other substances.

A voltage of 118 maintains an arc of one inch in an electric arc light, and requires 1 H.P. of electric energy, and fourteen sixteen-candle-power incandescent lamps represent the same amount of energy. It is not infrequent to find an arc light or twenty or more incandescent lights, or an equivalent energy from small motors connected to the pipe systems or the steel frame of the building. The effect of these strong currents is to set up a corrosion in the steel at some point where the current is interrupted on its return to the dynamo.

Under some one of their many developments, induced currents are strong enough to corrode metal, even if the main current or return current wires are adequate for their duty. Less than .005 volt establishes electrolysis, the amount of which is in proportion to the amperes present and not to the voltage.

Protection from the effects of the jump of the current, particularly in the lower parts of a steel frame, is rendered more uncertain, by reason of the disturbing action of electric currents from adjoining sources of generation. These currents finding their return to their source of generation obstructed from any cause, form a short or easier circuit that often lies through another dynamo's sphere of action. They invade its field and disarrange a return current system that at first might have been adequate for its duty, but is not able to withstand currents from its neighbor of subsequent installation.

Twenty or more of these electrical installations of different degrees of voltage, ampere, and work, are often placed within a comparatively small area. Many of these have been found to have a return wire system of inadequate size or of faulty insulation, and all of them subject to a wide range of fluctuation in energy due to the varying character of their separate work. With these influences at work at nearly all hours, it may be confidently expected that the near future will reveal some large and dangerous examples of corrosion in steel-framed buildings, from sources that thus far have received only a cursory consideration and no prevention.

Many instances are on record showing the erratic action and dangerous character of either stray or direct electrical currents. The United States Astronomical Observatory at Washington, D. C., though eligibly situated and free from the disturbing influences of a large city, had its magnetic observation department rendered useless by the stray electrical currents from a trolley line of street railway some three-fourths of a mile distant. This branch of science so closely associated with the daily needs and welfare of mankind, was paralyzed by the culpable indifference of a corporation to the requirements of science. It took an Act of Congress, carrying the imposition of a heavy fine to stop the nuisance. The Act not only prohibited the use of any underground water- or gas-pipes as means for returning the trolley-line currents to the power house, but also, forbade the connection of either pole of a railway dynamo in any direct manner with the earth.

Paints furnish neither remedy nor protection from electrolysis. Paints under catchy names are extensively advertised as being electrically inert, or insulating in charcter. Such names and statements are misleading and unreliable. No paint whose pigment is an oxide and again reducible by heat to a metal, is non-electric or passive to electrical influences in any degree beyond that due to the difference between the oxide and its metal, generally about 50 per cent, but is never *nil*.

Lampblack and graphitic carbon are the only pigments that are partially non-electric, and even with the use of these in a paint, the coating as an insulating substance is governed by the vehicle. The vehicles containing the resins, fossil gums and refined bitumen and combined by heat into a varnish, are the best for non-electric paints. It is quite unusual to find them in use on account of their cost, while the cheaper grades of resins and resin-oils used in the vehicle are only insulating up to a certain percentage, when they become conductors.

All of the vitreous class of pigments, such as slags, hard-burnt brick, tiles and slate, are conductors in their pulverized form, and usually act in a paint as the negative electrode to concentrate the electrical energy upon the covered ferric body. The thin coating of the vehicle, $\frac{1}{1000}$ to $\frac{1}{500}$ inch in thickness, is not resistant enough to but partially insulate the pigment, however effective the vehicle may be in mass or in heavier coatings that could not be applied cold with a brush.

Electrolysis inaugurated beneath such coatings, generally throws them off, or they act as a mask to conceal its ravages; while inferior coatings are rendered hard or porous from the decay of the vehicle or pigment.

*The following cuts and descriptions illustrate an instance of the effect of corrosion induced by stray electrical currents that caused the destruction of a water-works stand-pipe at Peoria, Ill., March 30, 1900, with the loss of life of two persons and the injury of fourteen others. The stand-pipe was 60 feet away from the other stand-pipes, and more than a mile away from the power station. Fig. 73 represents a sample of a steel sheet from the stand-pipe, showing the pitting in the sheet around the edges of the rivet-heads. The examination of the wreck of the stand-pipe showed that the whole inner surface of the vertical shell appeared to be thickly covered with blisters resembling in outward appearance the tubercules sometimes found inside of old cast-iron mains.

Fig. 73.—Pitting of steel stand-pipe sheet around the rivets.

A similar stand-pipe on the East Bluff was drained, and was found to be similarly pitted. This blistered covering, which was almost as thin as paper, was composed entirely of oxide of iron, and on brushing it away the black paint with which the stand-pipe had been originally coated was found beneath it. The paint was oftentimes almost unbroken, or, at least, very slightly cracked. When the

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* Excerpts from "Electrolysis of Underground Metallic Structures." A paper read by Mr. Darney H. Maury, Chief Engineer of the Peoria (Ill.) Water Works, before the American Water Works Association, May, 1900. *Engineering News*, June, 1900; also, *American Gas Light Journal*, July 30, 1900.

paint was brushed off the pit would be disclosed, considerably smaller in area than the surface covered by the blister. The surface of the metal in the pit was perfectly bright and clean and its fibre was clearly discernible. Many of these pits were more than $\frac{1}{8}$ inch in depth. They were slightly more numerous in the West Bluff stand-pipe than in the East Bluff stand-pipe, and were in both generally larger and deeper on the lower courses of the vertical shell.

The electrical examination relative to the stand-pipes was conducted mainly at the East Bluff stand-pipe, which was still in service. A flow of a part of the current from the railway-line was clearly traced through the earth to the anchor-bolts which held the stand-pipe to its foundation, as shown in Fig. 74, up these bolts and into the steel of the shell, and through the shell and from its inner surface to the projecting section of the 16-inch flanged cast-iron pipe which served as both inlet and outlet, and which connected the stand-pipe to the water-mains. The current was then traced along this pipe and along the mains to the power station. The deflections of the volt-metre needle were clearly traced to the railway current, being especially influenced by the cars on the line beyond the stand-pipe, and when the cars stopped running at night, the movement of the needle ceased. Where the current left the inner surface of the shell to pass through the water to the inlet pipe it made the pits already described.

Fig. 78 shows the interior surfaces of three sections of this inlet pipe, marked *A*, *B*, and *C*, respectively, the positions occupied by these sections originally being shown by the lettters *A*, *B*, and *C* in Fig. 74. An examination showed that strongly marked and numerous pits were inside the sections *A* and *B*, while the inner surface of the section *C* was practically as smooth and perfect as though new. When the condition of the inside of these three sections of pipe was first noted, it was hard to understand why *A* and *B* should be pitted, while *C* was unaffected. A closer examination, however, showed that in the flanged joints between the bottom sheet of the stand-pipe and *A* and *B*, respectively, corrugated copper gaskets were used, while the pipe *B* was separated from the pipe *C* by a thick rubber gasket; and that under the nuts and heads of the bolts holding the flanges together, there were grummets or wrappings of cotton wick soaked in tallow.

The result of this arrangement was, that the current which entered *A*, after passing through the water from the inner side of the shell of the stand-pipe, and which was trying to return along the inlet pipe and water-mains to the power station, encountered, at the joint

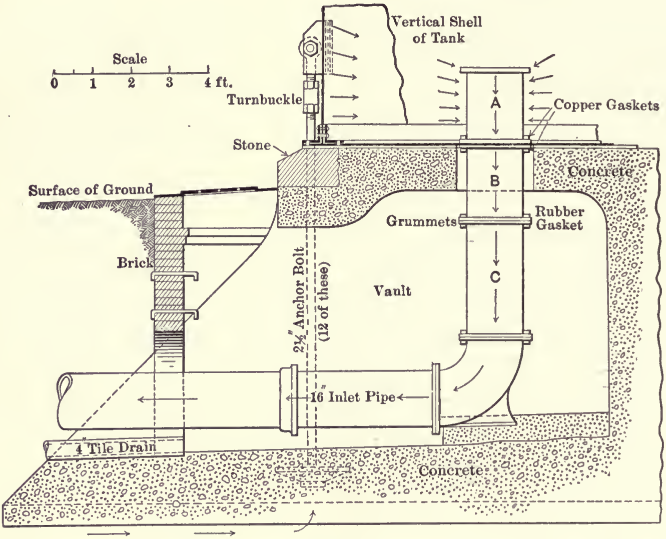

FIG. 74.—Partial section of Peoria stand-pipe, showing course of electrical current.

between *B* and *C*, the rubber gasket and the grummets. The effect of the gasket and grummets was to practically insulate the section *C*

FIG. 75.—Interior view of lengths of inlet to stand-pipe, showing pittings in *A* and *B*, and effect of the insulation of *C*.

from the sections *A* and *B*, and as none of these pipes were in contact with the ground, the current was compelled to leave the pipes *A* and *B* and travel through the water or along the slimy coating of oxide on the inside of the pipes around the joint between *B* and *C*, in order to continue on its journey. As the current was not leaving *C*, this pipe was not injured, but the current, in leaving the inner surfaces of *A* and *B*, did pit them, as shown in the photograph.

The experiments conducted since the destruction of this stand-pipe have determined that no manner of packing the joints in an underground cast-iron water- or gas-pipe line affects, only in a small degree, the difference in potential between the two ends of the connected pipes. Whether the joints were well or poorly calked, the pipes empty and dry, or full of water, clear or muddy, with scale on the pipe or clean surfaced, the drop of potential around the joint only varied from 0.0145 to 0.008 volt, and the general average resistance of the joints was about 96 per cent of the resistance of the whole line of pipe, and the resistance of the joints increased with age. Pitting was always observed where the shunt of the electric current left the metal to flow around the joint, and this corrosive action was as marked upon the inside surfaces of the pipes as upon the external surfaces; but from the conditions could not be observed. Wrought-iron pipes joined by the usual screw-thread and thimble connections were almost as universally attacked by electrolytic action at the joints of the cast-iron pipes. The difference in potential between the pipe and the socket, from their different arrangement of metallic fibres, resulted in the faster corroding of the pipe ends than the screwed socket or thimble.

Fig. 76.—Electrolytical pittings on 12-inch cast-iron water-main. (Current flowing from *A* to *B*.)

The joints in the cast-iron pipes, whether coated or not with the usual coal-tar preparations put on at the pipe-foundry, had little or no effect to insulate or protect the pipe from electrolytic corrosion, which generally showed in the form of blisters or like the usual tubercules formed on water-pipes by the action of water. These tubercules when broken, and the material under them analyzed, showed 22.3 to 23 per cent graphitic carbon and 47 to 47.7 per cent iron.

Fig. 77.—Electrolytical pittings no inside and outside of 4-inch cast-iron water-pipe.

The soil in which the pipes were embedded had received and was impregnated with the metal (iron or lead) corroded by the electric current, even to some distance from the pipe. In sections of pipe from 600 to 2000 feet long, there were several zones and centres of greater action than on the pipe in general, but they all centred toward the nearest generating dynamo, and were evidently localized at these points, from the greater amount of electrical energy cast off at the meeting and passing points and switching of the cars; contiguous lines of cars and currents from other sources all contributing in the most erratic manner to the corrosive result.

Mr. William Work, in a communication to the Institution of

Civil Engineers, 1901, reports the rapid corroding of wrought-iron service-pipes for water and gas, laid in a light, sandy soil. The water service-pipes corroded in seven years, so as to need renewal, and the gas service had almost completely disappeared at the end of ten years.

Analysis of the soil disclosed the presence of common salt, magnesium chloride, iron, alumina, silica, lime, and posphates. The town where the pipes were laid had no system of sewers, and during the summer season the streets were daily watered, and as the streets were level the water was quickly absorbed. The subsoil in which the pipes were laid was porous and alternated from dry to damp.

Carbonic acid was generated from the chemical action of the soil and attacked the pipes as stated. The trouble was confined to the wrought-iron service-pipes; the cast-iron pipe-mains to which the service pipes were connected were not affected in any noticeable degree. Similar pipe-services laid in neighboring towns where the soil was of a decomposed granite nature were comparatively uninjured after a period of twenty- even years.

Salt or lime in any soil in which pipes are laid necessarily prove active agents to promote corrosion, as they are hygroscopic in nature; and if alkaline substances are also present in the form of ashes and coal cinders, as they nearly always are in the soil of towns, the life of all wrought-iron work buried in it will be very short, even with the usual crude coal-tar coatings. Clay puddle around such pipes proves a good protection, as pipes so protected have been found practically uncorroded after forty years.

Mr. Chas. W. Rowe, Secretary of the Dayton, Ohio, Water Department, reports that the cast-iron water-mains laid in 1891 were found in 1900 so greatly affected by electrolysis as to endanger the water-supply of the whole city. Voltages of 4.5 were found in many parts of the pipe system.

The Annual Report of the Water Department shows that in 1899 579 feet of 6-inch pipe and 26 feet of 4-inch pipe were abandoned on account of electrolysis.

Mr. Rowe reports that in 1898 over 46,000 feet of the water-pipes from 4 to 16 inches in diameter were so seriously corroded by electrolysis from the trolley-line currents, that in some cases over one-half of their strength was gone. A 6-inch pipe became useless in five years. The pipes became coated with a graphite-like substance $\frac{1}{16}$ or more inch thick, the pebbles and stones in the ground near the pipes being plated with the same substance. About $\frac{19}{20}$ of the electric current used to drive the trolley cars was found to pass through the pipes and only $\frac{1}{20}$ passed by the street rails on its return to the dynamo.

Fig. 78 shows the electrolysis of a 4-inch cast-iron water-pipe at Reading, Pa.

Fig. 78.

No. 1. Laid 22 years or about 18 years before the advent of the trolley lines at the point where the pipe was laid.

No. 2. Laid thirteen months.

No. 3. Laid 22 years. Burst when uncovered for examination.

Fig. 79 shows a 16-inch cast-iron suction pipe; also a water main from Reading, Pa. The pipes are samples of those laid 300–800 and 1000 feet distant from the street trolley lines, and all were over two miles distant from the electric power station. The effect of the resistance of the joint packing is seen in the corrosion of the ring on the end of the pipes; also in the general corrosion at the ends where inclosed in the bell.

Fence nails were driven into the ends as easily as into a wooden post.

Flakes of corroded metal 3″×1″ in size and $\frac{1}{8}$-inch in thickness were of frequent occurrence in the Reading pipes.

"Electrolysis of Underground Water-Pipes" by Mr. F. C. Kelsey, Chief Engineer, of Salt Lake City, Utah, is a condensed report of the reports from the chief engineers of seven cities in the United States, of the presence of electrolysis in their water-supply systems.

FIG. 79.—16-inch cast-iron suction pipes (page 380).

Briefly stated, electrical currents of low potential, .001 volt, were found and were enough to establish electrolysis that under favorable conditions for the pipe might not have become serious in a limited period, but in the case of soils carrying salts and acids of decomposing materials the corrosion from electrolysis was materially accelerated and increased rapidly as the voltage rose to .01 volt. Currents of one-half volt destroyed a telephone cable in a few months. A minute quantity of soluble salt in the soil was enough to start the current and establish the electrolytic point or points in the metals, the corrosion of which continued as long as the current flowed. In all cases where the water-pipes or the metal-work of the building was positive to the earth or any surrounding object, the electric current flowed in that direction and electrolysis was established in the positive element of the couple, wherever it was situated. It was noticed in many cases that the lead service pipes and the lead-packing in the water-mains were corroded to such an extent that excessive leakage was the result, and the pipe-joints were no longer able to resist the pressure of the water when it was over 20 pounds. This corrosive action upon lead is of interest, as metallic lead has been generally considered electro-passive, and is used for the outer insulating covering for the cables in all underground conduits for electric lighting and power.

The Report of the Board of Commissioners of Electrical Subways, Brooklyn, N. Y., 1894, states that nearly 300 miles of lead-coated telephone cables were rendered useless by electrolysis from the trolley currents in that year. Many cases of corrosion were found where the lead cable was incased in pitch and other insulating compounds.

Mr. A. A. Knudson, E.E., reporting the electrolysis of a 48-inch diameter water-main in the city of Cambridge, Mass., found voltages of 25, and amperages of 30–50–80 and 90 at many points of the water-supply system.

Fig. 80, Electrolysis of a 6-inch cast-iron water-pipe at Providence, R. I. The pipe was ½-inch thick when laid and had been in service seven years.

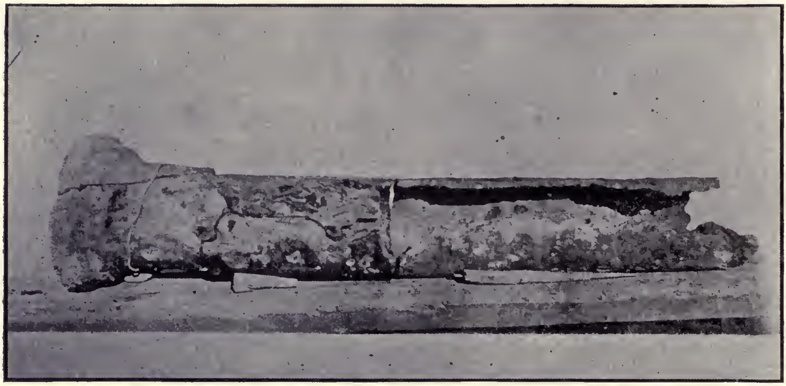

Fig. 80.—Electrolysis of a 6-inch cast-iron pipe at Providence, R. I.

Fig. 81 shows the electrolysis in one end of a steel truss for a trolley railway bridge at Providence, R. I. Both ends of both trusses were similarly corroded near the ground line.

The special committee of the American Water Works Association, to whom the subject of "Electrolysis of Underground Water-pipes" was referred, reported at the Richmond, Va., meeting of 1900, the result of their investigations: "That with the best bonded connection of the rails, including even the welded joint, it was impossible to secure the return of all of the current from a single trolley railway-line to its source of generation. Some of the current, under the law of divided currents, would invariably leave the rails and seek another source of return through near-by metal. The smallest measure of difference in potential between two metallic bodies was sufficient to produce and maintain electrolysis in one of them."

Fig. 81.—Electrolysis of a steel bridge truss.

Dr. Leybold's paper, "Electrolysis of Gas-pipes,"* states: "The pipes when laid were protected with canvas soaked in boiled coal-gas tar, and the destruction of the pipes was more rapid than where they were laid without the canvas coating. New pipes laid with canvas and tar coatings to replace the old ones were perforated into holes in seven to eight months."

The annual report of Mr. Wm. Jackson, City Engineer of Boston, Mass., states that $\frac{1}{1000}$ of a volt was sufficient to cause electrolysis, and some of the most serious cases of electrolytic action in the city water-mains were where only 1.5-volt pressure existed between the ground and the pipes.

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* *American Gas Light Journal,* September 30, 1901, p. 526.

Mr. L. Holman, Water Commissioner for the city of St. Louis, Mo., calls attention to the corrosion of 48-inch diameter water-mains in that city, that have been eaten away in many places for one-half inch, and could be cut as easily as plumbago. The danger arising from the bursting of such a pipe is apparent.

The practical effect in the corrosion of underground gas-mains and wrought-iron service-pipes, principally those of small diameter, is noted in the Official Reports of the Gas Bureau of the city of Philadelphia, where the loss from leakage in the form of unaccounted-for gas, for a period of ten years, was $5,750,000, and for the years 1891 to 1895 averaged two millions of cubic feet *per day.*

FIG. 82.—Exterior of a pipe injured by electrolysis, Springfield, Ill.

The Brooklyn Union Gas Company (Brooklyn, N. Y.) has about 760 miles of gas-mains of all sizes, and 280 miles of wrought-iron gas service-pipes. The latter and their fittings are found to be badly corroded wherever uncovered for examination. Electrolysis from stray electrical currents is manifest in many cases. Thirty-eight service-pipes in one street block were completely destroyed in three years. The cast-iron mains are reported to be generally in a good condition so far as electrolytic action is concerned, except in a few cases in what is called "the dangerous district;" that is, in the vicinity of the electric-station power-houses.

The loss of gas from all of the underground systems in this city in 1899 amounted to 13 per cent of the total yearly output (4,500,000,000 cubic feet), or a loss of 585,000,000 cubic feet.

Other cities in the United States show similar conditions in their gas systems. The ordinary corrosion of underground metal has been materially increased since the advent of electric street railways, however thoroughly the rails are bonded and used for the return current.

Lengths of pipe-mains over three miles long are reported to have corroded to such an extent that the whole pipe-line had deteriorated 50 per cent in four years. The voltage in this line was from 2 to 9 positive. At a voltage averaging 4.5, a 6-inch pipe became useless in five years.

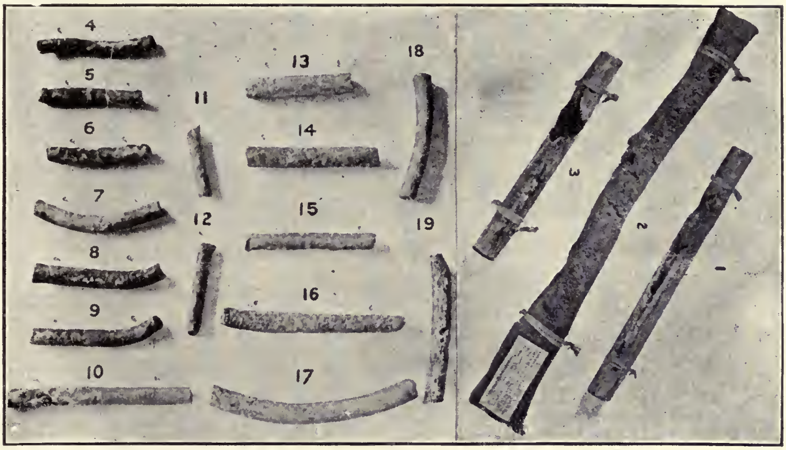

Fig. 83.—Lead water service-pipes and telephone-cable coverings in Brooklyn, N. Y.

Water-mains that were laid and tested to withstand a pressure of over 300 pounds to the square inch, at the end of four years leaked at almost every joint at 150 pounds' pressure. The voltage was 4.5, and the lead-joints were badly corroded.

Electrolysis of water-pipes at Kansas City, Mo.,* Mr. G. B. Wing, Superintendent of the Metropolitan Water Works, reports that specimens of the soil at a distance of two inches from some of the corroded pipe showed 4.67 per cent of iron, and at a distance of one foot, 2.65 per cent.

The corrosion of wrought-iron and lead pipes was more rapid than that of cast-iron pipes; the amount of corrosion in all cases *depended upon the amperage of the current.*

The electrical resistance of the ordinary lead and oakum-packed joints in the pipes was found to range from 110 to 200 times that of the pipe itself.

Variations in the resistance at the joints ranged from 0.0264 to

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* *Engineering Record,* Vol. XL, No. 11, August, 1899, p. 239.

0.0322 ohm, and in a section of 25 lengths of 4-inch pipe, averaged 0.11 ohm.

Fig. 84.—Effect of electrolysis on 6-inch cast-iron pipes, Kansas City, Mo.

"Wandering Electricity in New York City."* A report by Mr. A. A. Knudson, E.E., of an electrical survey of the section of New York City at Third Avenue and 135th Street, where a trolley-line had a terminus in front of an elevated-railway station. There was a difference of 2 volts, rising to 10 volts at times, between the trolley tracks and the nearest railway column, and a difference between the trolley tracks and the nearest gas-main of 5 volts.

In removing the rails of the trolley-line the effects of the passage of the current from them to the gas-main and elevated-railway structure were shown by the corrosion of the 70-pound rails. The base of the rails, originally 4 inches wide, was corroded away to $2\frac{3}{4}$ inches wide near the ends, the edges of the flanges being corroded to knife edges for several feet back from the ends.

Fig. 85 shows a section of the rails at one end.

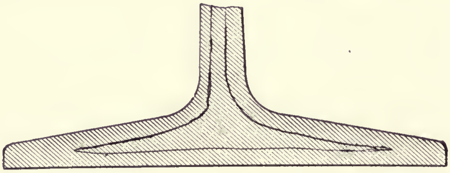

Fig. 85.—Electrolysis of a street-railway steel tee-rail.

The wrought-iron gauge-ties originally $1\frac{1}{2}'' \times \frac{3}{8}''$ in section were corroded completely away in the centre, and but one was found near the station that was unaffected from end to end.

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* *Engineering Record*, Vol. XXXVIII. No. 23, November 5, 1898, p. 500.

In the current at the terminal that passed to the water-mains and to the elevated-railway structure, there was a difference of from 2 to 2.5 volts. At one-fourth of a mile away the current all passed to the elevated-railway structure, ran a fourth of a mile, then returned to the water-pipes and changed again to the railway structure in about half a mile.

The same conditions were found to prevail on an opposite section of the elevated-railway structure, extending for about a mile in the opposite direction from the trolley terminal.

The difference in potential between the elevated-railway columns and the street-trolley rails and water-mains ranged from 1.30 to 1.50 of a volt, and indicated that the current came from an electric lighting station. It was also shown by the tests that a trolley-line using the rails, water and gas-mains for its return service, can spread the corrosive influences for a mile in either direction through the various subway conduits, pipes, and elevated-railway structures; also that the conductivity of a 50-pound street or tee-rail is about equal to a copper rod 1 inch in diameter, or five No. 000 B. and S. copper wires.

Tests applied to the Brooklyn Bridge suspension cables showed that generally there were 3 volts positive to the rails of the trolley railway on the structure. The effect of these currents upon the anchorages of the bridge led to a number of tests of the upper ends of the anchorage metal. The tests are believed by the bridge engineers to show "that no damage such as might be expected from *corrosion of underground metal* has thus far taken place."

A wise distinction between corrosion and electrolytic action. Had the question of the corrosion of the rails in the street tracks been put to the trolley-railway engineer corps, they would probably have been positive that no such corrosion was present or possible; in fact, they were indifferent to or ignorant of the corrosion until the examination by Mr. Knudson.

It required the public evidence of a half-dozen of broken suspension rods and panels of sunken railway tracks to convince the Brooklyn Bridge engineers that a serious case of neglect and corrosion existed in the structure, and had progressed far enough to be dangerous to it, ere a few long-neglected repairs were made.

That that neglect does not include the anchorage metal is by no means certain. There is absolutely no plan in the many suspension bridges erected that affords any practical means to ascertain the state of the lower members of the anchorage system, or of arresting corrosion or electrolysis in them if found.

Iron and steel bodies exposed to conditions similar to bridge anchorage metal have been found badly corroded within a few years after being placed in position, and there is no reason to infer that any bridge anchorage will be an exception.

The rate of corrosion from natural causes has been fairly determined. In anchorage work this will be increased by any electrical currents that may reach them, and it is inevitable that they do reach them, and no means of preventing it now exists.

The decay of metal by electrolysis has been approximately ascertained. The escape of the voltages and amperes used in street-railway service is twenty times that necessary to induce ferric corrosion and often more than twice as much as is necessary to decompose water in mass.

A current of 0.3 ampere is sufficient to corrode a lead covering to a cable or the lead in a pipe-joint. Electrical engineers report cases where the lead covering of cables has been destroyed in six weeks after laying.

A potential of $\frac{1}{1000}$ of a volt is all that is required to induce ferric corrosion two miles from the dynamo.

A difference in voltage of 20 volts has been found between the two ends of the Brooklyn Bridge cables, and the difference in voltage ranges from 0.75 to 3 volts at all hours and at all times in the day whenever tested, and is always found electro-positive to the ground.

So long as electricity obeys the known laws pertaining to its generation and transmission, it will select the line of least resistance, though it may not be the shortest in returning a major part of the current to its individual source of generation. It will also divide *en route*, pick up other electric currents in the most erratic manner, and deposit them in unexpected places, generally inaccessible for observation or repairs.

The large amounts of voltage and amperes used in railway-motor systems render stray electric currents more certain and electrolysis more constant, even if a "shunt" of the current from any adjoining bridge cable or structure were possible. At the present state of the electrical art this "cut-off" is practically not feasible.

The river that separates the two anchorages compels the bridge cables to act as conductors for the electric currents present at all times in the earth and air and never, or but momentarily, of the same potential.

Hundreds of electric installations of a great diversity of power surround these bridges and provide a cause of danger that at present, if known or suspected, has no remedy or safeguard.

The future results of electrolysis on all suspension bridges may as well be recognized now, rather than be left till the inevitable catastrophe befalls.

The corrosion of ferric bodies, *not* aided by electrolysis, is known to be progressive, being nearly 50 per cent more the second year than the first, and so on for each succeeding year.

During the construction of the Britannia Bridge over the Menia Straits, some rejected plates $\frac{7}{16}$ and $\frac{3}{4}$ inch thick, were left unprotected and exposed to the spray and wash of the sea. In two years they had corroded so that they could be swept away with a broom.

A few pieces of ironwork embedded in mortar or walled in some ancient building, or an old water-gate here and there, in some very favorable situation, may have remained uncorroded, but there is little unquestionable proof that iron or steel in the form adopted for bridges or structural frame-work will last more than two hundred years.

In the Niagara Falls and the Alleghany River suspension bridges, after about twenty-five years of duty, an inspection showed that some of the wires in the outer strands of the cables *outside* of the anchorages were corroded through, but the second and interior wires were sound. The reason assigned for the corrosion of the outer strand wires was that the "creep" of the individual wires under the varying strains due to the load and constant changes in temperature had worn away the boiled linseed-oil and other coatings applied when the wires were strung and allowed atmospheric moisture to reach them.

It is now proposed to abandon the boiled oil or paint coatings of the cables and to use a mixture of vaseline and plumbago. When the wires are strung and ready to bunch into strands and cables, all of the interstices are to be filled as far as possible with this stiff undrying mixture, that is to act as a lubricant for the inevitable creep of the wires, also as a protection from corrosion.

In all wire-wrapped cables there is an appreciable space between the wrapping and the cables, caused by the drying and shrinkage of the boiled oil coatings applied during their construction. The daily changes in temperature of the cable wrappings are greater than the mass of wires they cover, hence with the changes due to the extremes of summer heat and winter cold, they necessarily prove an element of weakness in providing a foundation for the paint coatings that are supposed to seal the cables water-tight.

Mr. Robert Mallet, C.E. (Dublin), made a report to the British Association in 1858 on paints for bridge and cable iron work: "That he had tested ten of the best and most reliable ferric paints and varnishes then known, and not one of them remained adherent and undecomposed for a single year under water. In moist air, and under conditions resembling English sea-coast fog, their state was not much better. The presence of moisture even to the extent of a partial saturation of the air, developed a fungus, the decomposition of which was almost as fatal to the life of a paint as immersion in sea-water."

Government authorities state that there are over 300 suspension bridges in Europe, of a great variety of spans and industrial importance; many of them having eyebars instead of wire cable suspensions. It is also stated that the life of the wire cables and anchorages have been found to be precarious, for oxidation was in progress in the interior of the cables, while the anchorages were weakened from the attack of some element "not at present defined" (evidently electrolysis). That there was no reliance to be placed on the preservation methods, or any certainty that they had effect on the life of the structure beyond twenty-five years.

The failure of the Angiers wire cable suspension bridge showed that it was impossible to keep the hydrate-of-lime coating used there in immediate contact with the anchorage metal. Moisture and earth acids, carbonic acid from the atmosphere reached the metal, and the lime-coating was practically useless to prevent corrosion.

M. Bernadeau in the "Annales des Ponts et Chausseur," 1881, refers to a bridge in which of the 150 wires forming a cable only 15 were in good condition, the rest were brittle as glass. The bridge had been in use less than forty years.

Two other suspension bridges of short span fell after twenty-six and twenty-eight years' duty.

The suspension bridge over the Ostrawitza River at Mährisch-Ostra, finished in 1851, failed in 1886 from a fracture of one of the anchor chains. The metal in the chain had thoroughly changed its character by corrosion, so that it could be crushed by the hand.

The anchor-bars in this bridge consisted of 12 links, one of which was completely corroded away and the others were reduced to about one-sixth of the original size. The original sectional area of the anchors was 24.4 square inches, but had corroded to about 4 inches. An official examination and report of the strength and condition of the bridge was made in 1885, one year before its failure, which stated that "The bridge has been examined in all its parts and is in good and safe condition." A squadron of Uhlans went down with the bridge.

An examination of the wire cables of a suspension bridge, where coal-tar and lime had been used to coat the wires, also to fill the interstices between them where the cables entered the anchorages, showed that these cables were wrapped with $\frac{1}{10}$-inch diameter wire and then a canvas jacket saturated with coal-tar and lime placed over them. After less than twenty years' duty the tar had partially decomposed and disappeared and the cavities were filled with a dirty, grayish liquid. The wrapping wire, also the seizing wire on the strands, were in many cases rusted through, and the cable wires deeply pitted. The damage to all the wires extended about three feet upward and outward from the cable anchorages. Beyond this there was a little rust, but no pitting, and still further from the anchorage the paint on the interior of the cable was gummy and undried.

*French engineers of reputation now prohibit the use of white-lead or any quick-drying paints on anchorage cables. The failure of a number of suspension-bridge cables in France was directly traceable to the use of that kind of paint. Chalking and cracking of the coating, owing to the ceaseless changes of temperature to which they and the cables were exposed, admitted water and held it, and corrosion of the wires at or near their lowest position in the cables was the result.

Euphorbium paints possessing elasticity, tenacity, and a quality that prevents them from drying bone-hard and becoming brittle, have proven the best paints used by French engineers for cable or other ferric work. Euphorbium being of a non-corrosive and anti-fouling nature, prevents the growth of atmospheric fungus, the decomposition of which produces an acid highly corrosive to iron.

Other resinous or varnish paints dried hard and brittle and soon cracked. Mastic proved to be the best of all the so-called copal gums for a bridge-cable varnish paint.

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*Le Génie Civil, 1881.

The failure of so many wire cable suspension bridges that have been in duty less than fifty years whose collapse can be attributed to corrosion or electrolysis and not to overloading, shows the imperative necessity of having the cable and particularly the anchorage metal *accessible for inspection at any time.* Corrosion of cables and metals in the air may be in part observed, but electrolysis occurring in the lower and hidden parts of the anchorage, and not reparable nor preventable, should be guarded against by a metallic connection at the anchor-plate end, that will lead off all electric currents and extinguish them in the earth and not in the metal of the structure. This connection can be renewed when corroded, and all shunts or attempted cut-offs of the current above the ground line avoided. In the case of divided currents, cut-offs have been found to be unreliable.

Cement coatings or concrete cannot retard electrolysis if any moisture is present. Mr. Eiffel found the iron rag-bolts placed in fortification masonry two hundred years ago, had enlarged from two to two and a half times their original diameter by rusting in the mortar in a dry location.

Rust once established, carries within itself the elements for a ceaseless life. Even in a glass bottle rust begets rust. Hydrated rust carries over 20 per cent of moisture, and so long as it can attack a fresh surface of iron and cast off the thin film of oxide as it forms, it will release enough oxygen to begin another cycle of action.

Farraday's law of the corrosion of metal in weak acidulated solutions and electrical energy applied to the anode is 1.0448 grains of iron per square foot, per ampere hour. The life of any ferric body can thus be approximately ascertained before its construction. The methods and means for its preservation should receive the most careful consideration of the engineer and others responsible for its protection. That its preservation is more difficult than its planning or construction does not remove this serious responsibility.

The borough of Brooklyn (New York City) has about 800 miles of water-mains of all diameters from 4 to 48 inches. Many of these pipes in the early construction of the water-works were cast in Glasgow from a firm close-grained cast iron which showed a white surface on fracture, indicating a large amount of combined carbon in the metal. Many miles of these pipes were also coated with Dr. Angus Smith's anti-corrosive compound, as before mentioned in this work. Previous to the year 1900 but few cases of electrolysis were reported in the water-mains of this city. The apparent freedom from electrolysis was attributed to the sandy soil in which the pipes were laid, also to the composition of the cast iron.

Scotch gray or forge iron was thought to be exempt from corrosion, and the Roebling bridge anchor-plates were made from this brand of cast iron and placed in the anchorages under this idea. But many of the pipes were cast in American foundries from American cast iron, and but little difference in their corrosion and that of the Glasgow-made pipes had ever been noticed. After the effect of corrosion by electrolysis had been noticed, to determine whether the composition of the cast iron had any power to prevent it, pieces were cut from the foreign and American cast-iron pipes, also from soft cast iron containing but little combined carbon and more graphite than the Scotch irons, and used as anodes in various electrolytic cells. The electrolytes consisted of samples of earth from various parts of the city, moistened with distilled, hydrant, and sea-water. The cells were exposed to the action of currents of different voltage and amperage.

In *every case* the anode was corroded, showing conclusively that there is *no immunity from electrolysis of cast iron used for water-pipes*, because of its chemical composition.

It was determined by the observation of the water-works' engineers that the tubercular corrosion on the water-pipes when unprotected other than by the usual thin coal-tar or bitumen pipe dips was at the rate of about $\frac{1}{1000}$ of an inch yearly, there being a difference in the rate of corrosion in the pipes of different metals, markedly in favor of the close-grained, white firm irons.

Summarizing the report of many other water-works' engineers, it appears that corrosion from electrolysis, tubercules, or from other causes is more rapid in wrought-iron than in cast-iron pipes, irrespective of the kind of soils they are buried in or to whatever influences they may be exposed.

The small amount of electrolysis in the city of Brooklyn gas- and water-mains was finally attributed by Prof. Samuel Sheldon * to the presence of the hard, thin, vitreous scale formed on them at the moment of casting in green sand molds, and that this scale was a non-conductor of electricity. This scale is similar to that noted on

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* Brooklyn Pol. Inst. Trans. American Institute of Electrical Engineers, May, 1900.

car-wheels and in connection with mining-pipes; it has been found to retard corrosion due to sulphureted water, and has been referred to on page 328.

A piece of the sand-coated pipe was covered with an insulating paint, but leaving exposed a small area of the silicate coating. This pipe was made the anode in an electrolytic solution. Less current flowed through the solution under a given E.M.F. than under similar conditions with an anode from the same piece of pipe, but exposing a clean iron surface of the same area to the same currents. In some of the experiments, no current at all passed the scale until the voltage was raised to a number of ohms. The water-pipes coated with Dr. Angus Smith's compound appeared to be less affected by electrolysis than the pipes not coated. The insulating quality of the compound added to the power of the silicate coating to resist the stray electrical currents of low potential. In certain districts of the city where high potential currents reached the pipes, electrolysis was present, but concealed by the firm and unbroken coating of Dr. Smith's and other heavy anti-corrosive coatings and was the more dangerous on this account.

In every city in which electric street railway, lighting, and power service is developed, there will be a number of districts corresponding to the number of power stations and plants for individual electrical generation. Each one of these installations will draw currents from its own district that can generally be very closely defined in the ordinary working of the station. But these boundaries become very irregular, daily and hourly, from the varying nature of the currents required for the work to be done in them respectively. A difference of potential has been noted—as high as 40 volts between different points in the same district or between adjoining districts. Hence these boundaries are always shifting to a greater or less extent at all times. It matters but little from which district the current reaches underground metal or what its potential, electrolysis is assured in every case.

Where electrical installations of a known amperage of 40,000 to 50,000 are in daily use, there will inevitably be some leakage of the direct and return currents as well as a certain energy in the induction currents, always present for the corrosion of metal, whether under ground or partly under ground and partly in the air. Perfect insulation from one or more or all of these currents is absolutely impossible. The best practice as it exists at present can only minimize their effect. While the writer has no desire to appear as an alarmist, the plain facts may as well be recognized now as hereafter, when the particularly dangerous character of stray electrical currents of low voltage and large amperage is forcibly presented to the public in the sudden collapse of some important structure or gas- and water-supply systems.

It is a false reliance that masonry, mortar, concrete, or cement are impervious to moisture and incapable of acting as an electrolyte such as would induce electrolysis. They are not insulating substances, or at the best only in the smallest degree under the most favorable circumstances. They are positively porous and in nearly every case, whether tested in large or small mass, are permeable to all waters or moisture and gases, and in but a few exceptional cases ever become thoroughly dry.

* A number of electric-light cable conduits in Paris were constructed of concrete, particular care being exercised in the selection of the hydraulic cement and sand used, as well as the ramming of it into place. The conduits were far above the water-line of the city's soil and were considered to be water-tight. The copper wires soon became covered with verdigris and copper chloride and so reduced in area that grounding and heating were of frequent occurrence from the normal currents of the service. A number of minor explosions also occurred, due to the gases formed by the decomposition of salt water that filtered through the cement when salt was strewn on the roadway over the cable conduit to melt the snow. The gaseous mixture contained oxygen, hydrogen, and chlorine, the latter gas being due to the chloride of sodium in the salt water. The leakage of the current furnished the electrical energy to decompose the salt water and fire the mixture, also to form the carbonate of soda and caustic soda that was deposited upon the copper wires.

Earthenware conduits were also used, but were not water-tight, and the same decomposition of the salt water and corrosion of the copper wires occurred as in the concrete construction, and their use was soon abandoned. The electric cable wires are now taped or covered with a bituminous compound to prevent electrolytic action.

President Learned, in his inaugural address to the New England Association of Gas Engineers, March meeting, 1902,† stated that

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* *L'Electricien*, 1892.

† "Electrolysis of Gas Pipes." *American Gas Light Journal*, March 3, 1902.

the conclusions derived from a large number of tests and observations of the effect of electrolysis on the gas-pipe systems in a number of cities in New England were: " That gas-pipes laid with lead joints have 15 per cent greater resistance to electric currents than water-pipes of the same diameter with similar joints. Screwed joints in wrought-iron pipes have about the same resistance as the lead joints in cast-iron pipes of the same diameter. The resistance of a Portland-cement joint, as ordinarily made, was from 15,000 to 20,000 times the resistance of a lead-caulked joint, comparing pipes of equal diameter. That the resistance of the cement joint depended in a great measure upon the amount of moisture that the cement takes up *after* setting.

" The conclusions drawn from the experiments made on gas-pipes of all diameters laid in short or long sections were: That all possible resistance should be inserted in the pipe mains by making the joints of some insulating or semi-insulating material, with an asbestos or tar-paper ring between the abutting ends of the pipe in order to break up the pipe-line into as many metallic units as possible, and isolate them from all other pipe or trolley systems, so far as practicable and mechanical conditions would allow. The pipes should be coated with a water-proof compound. The ordinary foundry-dip coating or painting with oil-paints had no appreciable effect to delay or diminish electrolysis of the pipes. Neat hydraulic cement coverings *were worthless* on account of the *porous nature* of the cement. It absorbed moisture, was inelastic, and easily scaled off the pipes by frost or mechanical injury.

" A covering made from 3 parts of dry clean sand and 2 parts of coal-tar boiled to a pitch at 660° F. made a mixture that was slightly elastic at ordinary temperatures, was thoroughly water-proof and when applied to the pipes to a thickness of 1½ inches, had an insulating resistance of over 1 million of ohms to the cubic inch. A short piece of 2-inch pipe covered with this mixture and immersed in a strong solution of water and soda ash for 8 hours, showed no signs of the absorption of any of the solution, nor had any decrease of electrical resistance been developed."

Mr. Robert Irvine, F.C.S., reports to the Chemical Society "that the cause of many disastrous explosions from the leakage of gas had been found to be due to electrolysis between the brass unions and other composition fittings and the iron service pipes and casings of the meter. Voltages between the brass and iron materials ranged from .3 to .5 of a volt, the iron in all cases being the electro-positive metal."

The corrosion by atmospheric exposure in the Brooklyn Suspension Bridge superstructure is deeply seated in every square foot of the structure and is beyond correction except by rebuilding it. It takes a corps of painters constantly at work three years to paint the structure, and the coating principally serves to mask the corrosion. The voltage of the electrical currents passing through the suspension cables has been referred to, but their corrosive effects upon the anchorage metal from the inaccessibility of the lower ends must always be a conjecture. These parts are beyond repair, and the electrical currents, whether from the trolley railway on the bridge, or from the scores of large installations surrounding the structure, are of large amperage, constant and uncontrollable in action. That they will not prove active agents of electrolysis is not in accordance with past experience.

In the other East River suspension bridges, where steel instead of masonry piers are used to carry the suspension cables and the superstructure, it is expected that the large metallic contact of the wire cables at the top of the steel towers will form a short circuit and ground for any electrical energy that may reach them from the railway, instead of using the anchorage metal for a terminal. This theory can only be determined after the bridge railway has been put in operation. The many points of junction of the bridge trestles with the masonry piers on both sides of the river may divide the trolley currents into a number of short circuits so as, in a measure, to protect the structure. But this cannot prevent the currents that come to the anchorage metal from the installations surrounding them, from using the cables for their transmission, as they provide the best and shortest metallic path for their ceaseless circuit.

A further fact relative to the electrolysis of the anchorage metal lies in its condition, even before any material strain other than the weight of the foot-path cables came to it. In the Williamsburg Bridge, the anchorage pits were carried down into the solid rock and near if not below the water level of the river. These were not sealed water-tight by any effectual method in laying the superincumbent masonry. The anchorage metal was put in place under a continual seepage of brackish water or that rendered alkaline from the cement, more or less pumping being required during the work. The anchorage metal, also the forged eyebars for the cable connections were indifferently cleaned, instead of being sand-blasted, and were painted with Smith & Co.'s "Durable Coating," the advisability of applying a baked japan coating being disproved on account of its cost.

When the chain of eyebars were ready for the cable construction, an anchorage pit was pumped dry and the eyebars inspected. Though the bars were covered with two coats of "Durable Coating," and in place only about two years, the paint was nearly destroyed, and corrosion over the whole surface of the bars wherever the water had reached them was virulent. The limited room in the pit and the close association of the eyebars together and to their bed, rendered the cleaning and repainting of them difficult and in many feet of their length impossible. A new coat of varnish paint, however, was applied in the damp atmosphere of the pit.

For the future protection of the eyebars it is proposed that when the bridge is completed and the chain of bars are bearing their load and have adjusted themselves to their permanent position, to paint them again and fill in between and around them for a foot or more with melted bitumen and to fill the pit with concrete. This plan does not reach the anchorage plates and metal in the lower end and inaccessible part of the pit. The corrosion serpent is only scotched (not killed) and will remain inactive for but a short time, or only so long as the concrete remains thoroughly dry, something impossible to maintain.

The bitumen coating insulates the eyebars so far as it can be applied and passes on whatever electrical currents may reach them from any source to the lower end of the anchorage, where the metal is not protected, corrosion in progress, and inspection almost if not quite impossible. To think that electrolysis will not take place in the metal at both ends of the bridge is to ignore facts already established. Electrolysis, or even corrosion from the contact of metal with moisture, in this case, is not the sin of the paint manufacturer; where to place the blame is not hard to find.

The introduction into marine service of appliances for the generation and use of electric power and light has developed a new field for electrolysis, that seriously endangers the efficiency and life of all vessels so equipped. An examination of the United States cruiser Brooklyn, for the purpose of determining the effects of a recent grounding of the vessel, has revealed the fact that electrolysis has attacked the inner skin or false bottom of the ship, and it is in such an advanced state of corrosion as to be practically destroyed. That she survived the grounding accident is a cause of wonder to the naval officers.

Electrolysis on board a steel ship is not unlike the same development by direct or stray electric currents in land or underground structures. Wherever a current of any potential leaves the metal, electrolysis is the result. In the case of naval vessels there is an enormous amperage present at all times and that cannot be returned to the dynamos, even with an increased capacity of the return-current wires over those employed for distribution of the current.

Divided and induced currents, also the electric energy developed by corrosion itself, will seek their own course either in returning to the dynamo or extinguishment in the ground connection. The latter, in the case of marine work, being water saline or foul in character, is a more efficient electrolyte than any earthy substance. Hence electrolysis in marine constructions willl naturally be more rapid and virulent than on a similar ferric area and current exposure on land or in underground structures.

As before stated, no paint or plastic coatings of the metal will prevent electrolysis. At best they may temporarily mask its progress, but it only requires a short time or a slight change in the conditions to reveal it.

Corrosion or electrolysis of marine metal can only be controlled by the use of some alloy of steel that will minimize the action, and by such an increase in the thickness of the parts of the ship exposed to corrosive influences as will for a time provide for any reduction of strength in the corroded parts or alloyed metal; also by a plan of construction that recognizes the possibility of the evil and provides that corroded members can be removed without practically rebuilding the ship. (See page 339 for Dr. Wurtz's protective method.)

Insulation of motors and their connections and the positive prohibition of the connection of any electric current, even of the smallest amount, to any part of the structure will reduce but not prevent the dangers of electrolysis, whether in marine or land constructions.

In either case, constant and thorough inspection of all ferric surfaces by an inspector who knows what to look for, and is competent to recognize it when it is found, is an essential. Even if the inspector cannot avert corrosion when found, at least the danger can be noted, watched, and a warning given when it is time to desert the ship. All of these essentials appear to have been absent in the case of the cruiser Brooklyn, and probably they are also neglected in all of the steel vessels in commission.

CHAPTER XXXV.

ANTI-CORROSIVE MARINE PAINTS AND ALLOYS.

The so-called marine paints are those applied to ships' bottoms to prevent corrosion, also those to prevent the growth of marine plants, barnacles, etc., and known as anti-corrosive and anti-fouling paints. The anti-corrosive marine paint is not applicable to ferric bodies in any other place than under water, as in the air they crack, flake, or crumble off rapidly. They draw the necessary oxygen to dry them from the water and carry large quantities of metallic salts and volatile driers to enable them to harden in an hour or so, an indispensable quality in a paint for a ship's bottom. One of the earliest patents in the arts was issued in 1670 for a tar and asphalt varnish for ships' bottoms, and since that time patents for marine paints have been issued, experiments and extended applications of them have been made by the thousand, and yet neither the corrosion nor the fouling of ships' metal has been rendered materially less than it was a hundred years ago.

Fossil resin varnishes prove to be the best vehicles for marine paints, whatever the composition of the pigments assembled with them. The nature of the pigments in these paints has a governing influence in exciting the galvanic action between themselves and the ship's metal, which action is speedily fatal to the coating as well as rapidly increasing the corrosion.

Corrosion in marine constructions is not only increased by the action of sea-water on the pigments and covered metal, but by the great porosity of the paints on account of the quantity of volatiles used. This porosity of the coating is also a prime factor in the decay of paint on land structures.*

The following tabulated results of a test of a large number of anti-corrosive coatings exposed to sea-water shows how inefficient nearly all of them are to meet the requirements of marine exposures. The baked coatings, Nos. 158, 159, 174, 175, 35, 113, 104, 105, 122, 124, not being applicable for a ship's bottom, however effective they

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* Pages 405, 406, 407.

may be for many other marine purposes, are practically eliminated for comparison with the other marine paints; but are useful to compare with the other coatings if used on land exposures where the corrosive influences are not so severe. Porosity in the baked coatings is eliminated and corrosion lessened whether the coatings are used on land or for sea-water exposure.

The Kauri and Zanzibar varnishes, composed of 20–30 or 40 gallons of linseed-oil to 100 pounds of fossil resin, were not as effective for preventing corrosion as where a pigment was added to the same quality of varnish, the order of merit for the pigments so used being carbon, zinc oxide, graphite, red lead, and iron oxide.

The test, while of value as a record of the comparative merits of the several coatings to resist corrosion, when exposed on a small plate to sea-water under absolutely uniform conditions for all of the coatings, still lacks the factor of their behavior when applied in mass of material to a ship or to land structures exposed to sea-air or sea-water.

The corrosion in the aluminum plates indicates that the metal to be non-corrosive must be alloyed with a metal lower in the electro-chemical scale than copper, in order to render aluminum of any practical value for constructions of any magnitude where strength or permanency are required.

See Mr. R. P. Hobson's (naval constructor, U. S. Navy) report to the U. S. Navy Department "On the Uses of Aluminum for Naval Work," published by the Navy Department, Washington, D. C., for other data on the corrosion of aluminum.

In some experiments of the "Alloys Research Committee" by Prof. Roberts-Austen, F.R.S., "samples of alloys containing 40 to 60 per cent of aluminum were kept a number of months before being analyzed. During this period they had spontaneously disintegrated to a powder. The powder was not oxidized, but consisted of clean metallic grains, probably resulting from chemical changes which had taken place in the solid alloys. Whether the iron and aluminum were in a state of solution, or were chemically combined when molten, they are evidently chemically combined in the metallic powder as attempts to melt it are unsuccessful, which indicates the formation of an infusible compound. The two metals may have been too hot to unite thoroughly when in a molten state, but a long-continued proximity at a lower temperature affected their chemical union."

M. Le Chatalier, in a paper read before the Académie de Sciences, Paris, stated that equal parts of aluminum and copper were fused together in a crucible. The ingot was placed in a solution of common salt and lead chloride for twenty-four hours with a view of dissolving out the uncombined aluminum. No change in the ingot was apparent at the end of this time. The ingot was removed from the bath, washed, and dried. Twelve hours afterwards the ingot was found to be reduced to powder from the spontaneous oxidation cf the alloy. A similar ingot not immersed in the saline bath was unchanged at the end of a month.

Three small aluminum boats, used by Mr. Wellman in his 1894 polar expedition, soon after they were brought back could be crumbled in the hand.

Corrosion of Ferric Alloys.

The influence of copper and nickel alloyed with wrought iron and soft steel was made the basis of a paper by Mr. F. H. Williams, C.E., read before the Engineering Association of Western Pennsylvania. The paper was based upon experiments made in the line of some recent investigations by Mr. H. M. Howe, as given in his paper, "Relative Corrosion of Wrought Iron and Soft Steel and Nickel Steel," read before the International Congress, Paris, on Testing Materials.*

"In prosecuting the tests, Mr. Williams selected four samples of steel, viz.: A, an ordinary soft Bessemer steel; B, C, D, soft Bessemer steels to which copper had been added in the converter so that they contained respectively 0.078, 0.145, 0.263 per cent. In addition, another set of test materials, consisting of one soft Bessemer-steel sample and four of wrought iron, were similarly alloyed, sample number 4 of wrought iron having 0.393 per cent of copper. All the samples were brought to the same dimensions, then weighed and suspended in a frame, so that they could all be dipped simultaneously in water and left to dry in the open air, this treatment being repeated frequently each day for a month. The daily increase in weight due to oxidation was small, but of such a persistent character as to indicate the retarding influences of the copper upon the corrosion. Finally, where there appeared a tendency of the oxide to scale off, the treatment was suspended, the samples dried, cleaned from all oxide, and weighed. The loss in the original weight of the samples is tabulated, viz.:

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* *Engineering Record,* December 1, 1900, p. 519.

Loss from One Month's Exposure to Atmospheric Corrosion.

A. Soft Bessemer steel	1.85 per cent.
B. " " " with 0.078% copper	0.89 "
C. " " " " 0.145% "	0.75 "
D. " " " " 0.263% "	0.74 "
Soft Bessemer steel, second sample	1.65 "
Wrought-iron sample number 1 with 0.078% copper	0.76 "
" " " 2 " 0.145% "	0.80 "
" " " 3 " 0.263% "	0.87 "
" " " 4 " 0.393% "	0.53 "

"Mr. Howe's experiments indicated that in large plates of metal containing nickel in approximately the same proportions as the above examples, and exposed for a considerable time, the corrosion was similarly retarded. The introduction of a small amount of copper or nickel into soft steel can be easily effected, and their presence within the amount necessary to obtain the above results has been demonstrated not to be prejudicial to its physical properties. The data here presented, while not showing that corrosion of ferric bodies can be wholly prevented by alloying them with copper or nickel, they do indicate that a soft steel can be made capable of resisting corrosion quite as well as wrought iron and thus settle the debate about their relative corrosibility now so much in question."

In the case of aluminum, the natural field for its use appears to be in marine construction, where lightness is an essential requirement, particularly in naval construction, where economy in weight has a vital relation to military efficiency. But its corrosibility, if exposed to sea-air or sea-water, has demonstrated its unfitness for any structure exposed to these influences.

Alloys of copper with aluminum increase the corrosion, which is greater as the amount of copper is increased. With 2 per cent of copper the increase of corrosion is markedly greater than with the pure aluminum, and where 5 per cent of copper is used, as in the case of the Yarrow torpedo-boats, on account of the great increase in the strength of the metal, the corrosive effects were disastrous, and caused an abandonment of the metal for French naval work. The interest in this feature is special, as the aluminum needs an alloy to increase its strength, and copper appears to be the one metal best suited for this purpose, though other metals are available. The increased corrosion due to the presence of copper is attributed to the fact that the two metals are so widely separated in the electrochemical scale that an alloy made from them contains the necessary elements for a strong galvanic action that soon destroys the integrity of the metal. This action is also developed where copper in any form is brought into contact with iron or steel for any exposure.

The action of sea-water on the corrosion of various metals has been investigated by the German engineer, Digel, who reports "that alloys of copper 20 per cent and nickel 42 per cent are not very rapidly corroded. Adjacent masses of iron, copper, or copper alloys render the copper and nickel alloys somewhat immune against sea-water corrosion, the above-mentioned metals being rapidly corroded.

"Copper and zinc alloys are corroded almost uniformly over the surfaces exposed to the sea-water. When the zinc exceeds 24 per cent of the alloy, it is leached out, leaving a brittle porous mass of copper. Adding 15 per cent of nickel to the alloy prevents this leaching action.

"Very pure electrolytic copper, in contact with ordinary commercial copper (99 per cent pure), is very rapidly corroded by sea-water. When the two coppers are *not* in contact, they corrode about alike. Both of the above brands of copper when annealed are more rapidly corroded than when rolled. Copper coated with zinc is temporarily protected from sea-water, but when the zinc has been dissolved, the corrosion of the copper is increased rapidly.

"Electrolytic copper that had its surface oxidized in places developed rapid galvanic action in the clean spots. Copper pipes brazed into vessels or into each other are subject to corrosion in the brazed joints from galvanic action.

"One-half of 1 per cent (0.5) of arsenic in metal greatly retards corrosion.

"Wrought iron and steel of various methods of manufacture are greatly influenced in corrosibility by the amount of phosphorus contained in them. With 1 per cent of phosphorus present the corrosion was a little over one-half as great as in the case where the iron was free from phosphorus. When two pieces of phosphorus iron or steel were in contact, the sea-water corroded the low phosphorus metal from two to five times as fast as the high-grade metal.

"Iron alloyed with nickel showed the same behavior.

"The normal corrosion of single plates of metal was less as the percentage of nickel increased. When two plates differing in the contained nickel were brought into contact, the plate higher in nickel was almost completely protected from corrosion."

*TABLE SHOWING RESULTS OF TESTS OF PROTECTIVE COATINGS APPLIED TO STEEL AND ALUMINUM PLATES IMMERSED FOR THIRTEEN MONTHS† IN SEA-WATER AT BROOKLYN NAVY-YARD.

No. of Plate.	Character of Vehicle.	Character of Pigment.	Application and Preparation.	Condition of Plate and Coating.
			Aluminum Plates.	
151	20 Kauri varnish	None.	Air-dried.	Edges blistered; no considerable corrosion.
152	30 “ “	“	“	Covering one-half gone; much corrosion.
153	40 “ “	“	“	“ mostly gone; badly corroded.
154	I X L No. 2 varnish	“	“	“ half gone; not badly corroded.
155	Spar varnish	“	“	“ mostly soft; some corrosion, not deep.
156	“ “	“	“	Somewhat more corroded than plate 155.
157	Durable metal coating	“	“	Hard; no corrosion; 20% blistered at edges.
158	Pipe coating		Baked.	Good condition.
159	“ “		“	“ “
160	30 Kauri varnish	White zinc.	Air-dried.	Quite hard; top, good condition; bottom, blistered.
161	40 “ “	“	“	Good condition.
162	30 Zanzibar varnish	“	“	Excellent condition; no corrosion; no blisters.
163	Spar varnish	“	“	Several large blisters; not deeply corroded.
164	20 Kauri varnish	None.	“	Covering three-fourths gone; badly corroded.
165	30 “ “	“	“	“ badly destroyed; much corrosion.
166	40 “ “	“	“	“ considerably blistered; not much corrosion.
167	I X L No. 2 varnish	“	“	“ “ “ somewhat corroded.
168	Spar varnish	“	“	Coating soft; some blisters; not badly corroded.
169	Durable metal coating	“	....	Hard; considerably blistered; very little corrosion.
170	30 Kauri varnish	White zinc.	Air-dried.	“ few blisters; some corrosion.
171	40 “ “	“	“	Considerably blistered and corroded.
172	30 Zanzibar varnish	“	“	Hard; no corrosion; no blisters.

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* *Engineering News*, Vol. XL, No. 4, July 28, 1898.

† The twelve plates from the 1896 test were immersed six months longer than the others, or nineteen months altogether.

TESTS OF PROTECTIVE COATINGS—*Continued.*

No. of Plate	Character of Vehicle.	Character of Pigment.	Application and Preparation.	Condition of Plate and Coating.
			Aluminum Plates.	
173	Spar varnish.	White zinc.	Air-dried.	Hard; no corrosion.
174	Pipe coating.		Baked.	Good condition; no corrosion; no blisters.
175	“ “		“	“ “
...	Mitchell's.	White enamel.	....	Excellent condition.
			Steel Plates.	
251	40 Kauri varnish.	Ultramarine blue.	Air-dried.	Many small blisters; little corrosion.
252	Raw oil.	“	“	Coating practically gone; uniformly corroded.
253	20 Kauri varnish.	Graphite.	“	Blistered slightly; very little corrosion.
254	30 “ “	“	“	Few small blisters; no corrosion.
255	40 “ “	“	“	Many small blisters; no corrosion.
256	Raw oil.	“	“	Coating destroyed.
257	20 Kauri varnish.	Keystone.	“	Many pin-head blisters, but generally good.
258	30 “ “	“	“	Pin-head blisters; no corrosion.
259	40 “ “	“	“	“ “ “ “
260	Raw oil.	“	“	Coating destroyed; badly corroded.
261	20 Kauri varnish.	Red iron oxide.	“	Blistered some; not badly corroded.
262	30 “ “	“	“	Many small blisters; some corrosion.
263	40 “ “	“	“	Many pin-head blisters; some corrosion.
264	Raw oil.	“	“	Coating practically destroyed; badly rusted.
265	“ “	Red lead.	“	“ mostly gone; considerable corrosion.
267	“ “	Prince's metallic.	“	“ practically destroyed; badly rusted.
268	“ “	Purple iron oxide.	“	“ “ “ “ “
269	Eureka paint.		“	“ badly destroyed; badly rusted.
270	Detroit graphite paint.		“	“ destroyed; badly corroded.
272	Bowles' paint.		“	Good condition; few blisters.
273	Rahtjens paint.		“	Coating badly gone; considerable corrosion; few barnacles.

TESTS OF PROTECTIVE COATINGS—*Continued.*

No. of Plate.	Character of Vehicle.	Character of Pigment.	Application and Preparation.	Condition of Plate and Coating.
			Steel Plates.	
274	McInnis paint		Air-dried.	Very good condition; no barnacles.
275	International Holtzapfel		“	Coating badly gone; considerably corroded; small barnacles.
277	Red lead and white zinc		“	Soft, gone in spots; corroded on edges
278	“ “ “ “ “		“	“ “ “ “ “ “ “
281	20 Kauri varnish	None.	“	Discolored on edges by rust; not deeply rusted.
282	30 “ “	“	“	Small blisters; not deeply corroded.
283	40 “ “	“	“	Pin-head blisters; not deeply corroded.
284	30 Manila varnish	“	“	Numerous small blisters; not deeply corroded.
285	30 Zanzibar varnish	“	“	Many pin-head blisters; little corrosion.
286	Spar varnish	“	“	Badly destroyed; considerable corrosion.
287	I X L No. 2 varnish	“	“	Many pin-head blisters; not much corrosion.
288	Raw oil	“	“	Coating destroyed; badly corroded.
289	Durable metal coating		“	Many small blisters; little corrosion.
			Steel Plates Reimmersed after 1896 *Test.*	
1	20 Kauri varnish	Flake white.	Air-dried.	Rusted on edges; discolored; good condition otherwise.
2	20 “ “	“ “	Baked.	“ “ “ “ “ “ “
16	20 Manila varnish	White zinc.	“	Some blisters; one side considerably corroded.
18	8 “ “	Flake white.	“	Hard; pretty good condition.
20	30 Zanzibar varnish	White zinc.	“	No blisters; no corrosion.
22	20 “ ‘	“ “	“	Few blisters; some corrosion; hard.
35	Sabin Process pipe-coating enamel			Some corrosion on one edge; otherwise good condition.
			Aluminum Plates Reimmersed after 1896 *Test.*	
113	Sabin Process pipe-coating enamel			Two small blisters; otherwise good condition.
104	White zinc ground in varnish		One side baked.	Three or four small blisters; otherwise good condition.
122	“ “ “ “ “		“ “ “	“ “ “ “ “ “ “ “
105	Chromium oxide ground in varnish		“ “ “	Few small blisters; generally excellent condition.
124	Spar varnish		“ “ “	Two or three small blisters; no considerable corrosion.

CHAPTER XXXVI.

MISCELLANEOUS TABLES AND DATA.

Pigments and Inert Substances.

Substance.	Symbol.	Specific Gravity.
Asphaltum		1.8—1.39—1.04
Alumina oxide (clay)	AlO	2.75—2.6
Anthracite coal		1.70—1.35
Bituminous coal		1.318—1.277
Bitumen		1.16—0.83
Barytes (heavy spar)	$BaSO_4$	4.7—4.3
Brick-dust		1.50—1.30
Cement, hydraulic, common		1.6—1.5
“ “ Portland		1.51—1.25
“ “ Rosendale		1.00—0.96
Charcoal in bulk	C	0.441
“ oak	“	0.336—0.331
Coke, natural, Virginia	“	0.746
“ hard foundry	“	0.800
“ gas retort	“	0.70
Cobalt (blue)		8.6—8.5
Coal-tar (gas retort)		1.1—1.00
Chalk, red and black	CaO	2.8—2.2
“ whiting, Spanish white		2.1—1.8
Clay (see Terra-Alba)		2.71—2.56—1.93
Carbon (diamond)	C	3.529—3.55
Feldspar		2.8—2.5
Flint		1.93
Gneiss and granite		2.8—2.76—2.62
Glass		2.782—2.5
Graphite, amorphous		2.768—2.208
“ flake or foliated		1.40—1.21
Gypsum, native sulphate of lime (hydrated)	$CaOSO_3+H_2O$	2.5—2.38
“ (calcined) plaster of Paris	$CaOSO_3$	2.4—2.08
Lampblack	C	0.44—0.80
Lime (quick)	CaO	0.88—0.8
Limestone, common gray	$CaCO_2$	2.7—2.6
“ Carrara marble	“	2.717
Lead, metallic	Pb	11.44—11.07
“ white, carbonate	$PbCO_3$	6.480—6.465
“ chromate	$PbCrO_3$	5.2—4.61
“ hydrate	$Pb(OH)_2$	7.00—6.6
“ sublimed	$PbSO_4$	6.258
“ sulphite (dark color)	PbS	6.43
“ sulphate (white color)	$PbSO_4$	7.13
Litharge	PbO	9.00—8.50

PIGMENTS AND INERT SUBSTANCES—*Continued.*

Substance.	Symbol.	Specific Gravity.
Lithopone (zinc sulphate)	$PbSO_4$	4.2
Red lead (minium)	Pb_3O_4	9.07—8.94—8.06
Marl		2.4—1.73
Mica		3.1-2.75
Masonry, brick or tile		2.0—1.79
Magnesia, carbonate	$MgCO_2$	3.2—2.72—2.4
Manganese dioxide or pyrolusite	MnO	4.97—4.816
Ochre		4.6-3.2
Iron, metallic	Fe	7.84—7.77
" oxide (red rust), 70% iron, 30% oxygen.	Fe_2O_3	5.77
Iron ore, red and brown; hematite, specular and columnar; spathic, etc.	Fe_2O_3	5.334.62 4.20—3.80
Black magnetic oxide, 72.413% iron, 27.587% oxygen	Fe_3O_4	6.062
Phosphate of lime (basic steel furnace slag)	$Ca_4(PO_4)_2$	3.5—3.8
Pitch		1.152
Quartz		2.7—2.64
Resin	$(C_{20}.H_{40}O_2)$.	1.089—1.07
Orange or Paris red	$PbCO_2$	8.1—7.5
Sand from quartz		1.76—1.44
Silica (crystalline)	$SiSO_2$	2.8—2.5—1.9
" (amorphous)	$SiSO_2$	2.34—1.9
Silex (floated)		2.8—2.3—1.8
Slate		2.9—2.7
Slag, furnace		3.6—4.3
Soapstone or steatite		2.8—2.65
Sulphate of iron (copperas)	Fe_3SO_4	5.175.04
Sulphur, native ore, melts at 115° to 120° F.	S	2.03—3—2.05
Spanish brown (oxide of iron and clay)		2.2—2.1
Umber (argillaceous brown hematite iron ore).	$2Fe_3O_3,SiO_2+H_2O$	2.4—2.2
Terra alba, China, pipe and potters' clay, complex oxides of all metals		2.71—2.56 2.4—1.92
Vermilion (mercuric sulphate)	HgS	8.91-8.1
Vermilionette (mixed color)		7.5—7.0
Zinc metallic	Zn	7.0
" carbonate	$ZnCO_3$	4.4—4.0
" oxide or zinc white	ZnO	5.6—5.4
" sulphide (dark color)	ZnS	4.2—3.9
" sulphate (white color)	$ZnSO_4$	5.3—5.0

The trade or commercial color pigments number 245, viz.:

Black	22	Green	46
Blue	28	Red	50
Brown	24	White	36
Gray	3	Yellow	36
	77		168

Characteristics of Metallic Bases of Pigments.

Metal.	Symbol.	Combining Weight.	Specific Gravity.
Antimony	Sb	120.4	6.86—6.36
Aluminum	Al	27.1	2.71—2.56
Arsenic	As	75.1	5.96—5.52
Barium	Ba	137.4	6.85
Bismuth	Bi	200.0 208.1	9.90—9.74
Calcium	Ca	40.1	1.58
Cobalt	Co	59.	8.6—8.5
Copper	Cu	63.6	8.92—8.69
Iron	Fe	56.	7.77
Lead	Pb	206.9	11.38
Magnesium	Mg	12.	1.743
Manganese	Mn	55.	4.97—4.82
Mercury	Hg	200.	13.62—13.58
Nickel	Ni	58.3	8.93—8.28
Potassium	K	39.	0.865
Phosphorus	P	31.	1.823—1.777
Silicon	Si	28.4	2.8–2.5
Sodium	Na	23.	
Sulphur	S	32.1	2.05— 2.033
Gold	Au	197.2	19.36—19.245
Silver	Ag	107.7	10.51—10.474
Tin	Sa	119–117.8	7.409–7.300
Zinc	Zn	65.4	7.13—7.0
Red and brown hematite and specular iron ore; iron=70%; oxygen=30%	Fe_2O_3	56 and 16	5.4–5.3 4.65–4.2
Magnetic or black oxide of iron; iron=72.413%; oxygen=27.587%	Fe_3O_4	56 and 16	5.6—5.3

Gases and Elements that Cause the Decay of Paint.

The principal gases and elements that affect all paints at a temperature of 60° F. and under one atmospheric pressure are:

Substances, Gas or Vapor.	Specific Gravity.	Number of Cubic Feet per Pound.
Alcoholic vapor	1.589	8.27
Ammonia " NH_3	0.597	20.95
Atmospheric air	1.00	13.11—13.14
" " saturated as fog at 80° F.	1.0236	12.80—12.831
Benzine vapor, C_6H_6	2.7	4.78
Bisulphide of carbon, CS_2	2.6447	4.85
Carbonic oxide, CO	0.9727	13.57—13.60
Carbonic-acid gas, CO_2	1.529	8.594
Ethelene or olefiant gas, C_2H_4	0.9784	12.580
Hydrocarbon (illuminating gas), CH_2	0.302	33.112
Natural gas	0.54	24.335
Nitrogen, N	0.9714	12.752
Oxygen, O	1.056	11.887
Hydrogen, H, 16 times lighter than air 14½ " " " oxygen	0.06926	189.552—189.70
Marsh gas, C_2H_4	0.559	23.479
Phosphoric acid, $3HOPO_5$		
Phosphorated hydrogen, PH_3		
Steam, saturated, 212° F.	0.49959	26.36
" gaseous	0.622	21.077
Turpentine vapor	2.76	4.76
Smoke of bituminous coal	0.102	
" " coke	0.105	
" " wood	0.09	
Sulphurous-acid gas, SO_2	2.213	5.90
Sulphuretted hydrogen, H_2S	0.177	74.422
Sulphuric ether	2.586	5.08
Wood-alcohol vapor, CH_4O_2	0.812	boils at 140° to 150° F.

Oxygen in Pigments.

Paint-trade literature bears so persistently upon the point that red lead, from the great amount of oxygen it contains is not only self-destructive, but will destroy all other paints of which it forms a part; also, that by reason of this inherent element, it acts the part of a carrier for an additional amount of oxygen that it may collect from other sources, the joint effect resulting in an early destruction of the coating; also in promoting corrosion of the covered surfaces. The following comparison of the amount of oxygen in a number of pigments and so-called inert substances in common use in paints is of interest upon this point:

Substance.	Symbol.	Metallic, Per Cent.	Oxygen, Per Cent.	Other Elements, Per Cent.
Litharge	PbO	92.822	7.178	
Red lead	Pb_3O_4	90.63	9.37	
White lead (carbonate)	$PbCO_3$	77.516	17.987	Carbon, 4.497
Sublimated lead	$PbSO_4$	71.831	18.561	Sulphur, 9.608
Sulphate of lead (native ore)	$PbSO_3$	72.09	16.746	" 11.164
" " " (pigment)	$PbSO_4$	62.283	21.145	" 10.572
Sulphite of lead	PbS	86.57	00.00	" 13.43
Zinc oxide	ZnO	80.344	19.656	
" sulphide	ZnS	67.077	00.00	" 32.923
" sulphate	$ZnSO_4$	40.495	39.670	" 19.835
" carbonate	$ZnCO_3$	52.153	38.278	Carbon, 9.569
Whiting, chalk	CaO	71.479	28.52	
Iron oxide	Fe_2O_3	70.00	30.00	
" magnetic oxide	Fe_3O_4	72.413	27.587	
Barytes	$BaSO_4$	65.172	22.097	Sulphur, 12.731
Gypsum	$CaOSO_3$	41.20	35.28	" 23.52
Manganese dioxide (pyrolusite)	MnO_2	43.161	56.839	
Vermilion	HgS	86.207	00.00	" 13.793
Umber (hydrated),	$2Fe_2O_3.SiO_2 + H_2O$	55.735	34.67	Silicon, 9.594

COMBINATIONS OF OXYGEN WITH CARBON AND SULPHUR.

Substance.	Symbol.	Oxygen, Per Cent.	Carbon, Per Cent.	Number of Cubic Feet of Gas in One Pound.
Carbonic oxide	CO	57.14	42.86	13.57
Carbonic acid	CO_2	72.73	27.27	8.59
Carbon trioxide	CO_3	80.00	20.00	6.47
Sulphuric oxide	SO	33.264	Sulphur. 67.736	
Sulphurous acid (the acid of burning sulphur)	SO_2	50.00	50.00	3.848
Sulphuric acid	SO_3	60.00	40.00	3.569
" " anhydrous	SO_4	66.6	33.4	2.944

CHANGES IN PIGMENTS DUE TO ATMOSPHERIC INFLUENCES.

Red lead (Pb_3O_4) = lead, 90.63 per cent; oxygen, 9.37 per cent.
Specific gravity, 9.07. 682 grammes, volume = 75.2 c.c.
Upon exposure to hydric-sulphide gas in the atmosphere it
Changes to
Red-lead sulphide (PbS) = lead, 86.61 per cent; sulphur, 13.39 per cent.
Specific gravity, 7.13. 714 grammes, volume = 100.1 c.c.
Increase in volume, 24.9 per cent.

Zinc oxide (ZnO) = zinc, 80.344 per cent; oxygen, 19.656 per cent.
Specific gravity, 5.42. 81 grammes, volume = 14.9.
Upon external atmospheric exposure, absorbs carbonic acid and
Changes to
Zinc carbonate ($ZnCO_3$) = zinc, 52.153 per cent; { oxygen, 38.278 per cent;
carbon, 9.569 per cent.
Specific gravity, 4.44. 125 grammes, volume = 28.
Increase in volume nearly double.

White lead ($PbCO_3$) = lead, 77.516 per cent; { oxygen, 17.987 per cent;
Hydrated carbonate; carbon, 4.4972 per cent.
Specific gravity, 6.480.
Absorbs carbonic acid from the atmosphere and
Changes to
Subcarbonate of lead ($PbCO_4$) = lead, 73.138 per cent; { oxygen, 20.62 per cent;
carbon, 6.242 per cent.
Specific gravity, 6.40.
Absorbs sulphurous-acid gas and
Changes to
Sulphide of lead (PbS) = lead, 86.57 per cent; sulphur, 13.43 per cent.
(Dark color.)
Specific gravity, 6.45.
Absorbs more sulphurous acid and
Changes to
Sulphate of lead ($PbSO_4$) = lead, 68.283 per cent; { oxygen, 10.572 per cent;
(Light color.) sulphur, 21.145 per cent.
Specific gravity, 7.13.

Barytes (heavy spar) ($BaSO_4$) = Ba, 65.172 per cent; { oxygen, 22.097 per cent;
Native sulphate of barium; sulphur, 12.736 per cent.
Specific gravity, 4.7 to 4.3.
Absorbs carbonic acid from the atmosphere, that releases the one atom of sulphuric acid (SO_3) in its composition and
Changes to
Barytes carbonate ($BaCO_3$) = Ba, 69.10 per cent; { oxygen, 24.72 per cent;
carbon, 6.18 per cent.
Specific gravity, 4.1. Change in volume, 5 per cent.

Gypsum (native) } $CaOSO_3$ = calcium, 41.20 per cent; { oxygen, 35.28 per cent;
Sulphate of lime } sulphur, 23.52 per cent.
Specific gravity, 2.4 to 2.08 (calcined).
When calcined, it releases sulphuric acid and absorbs carbonic acid from the atmosphere and
Changes to
Carbonate of lime } CaO = calcium, 71.478 per cent; oxygen, moisture and carbonic acid, 28.522 per cent.
Chalk or whiting }
Specific gravity, 2.2 to 2.8. Increase in volume, 5 per cent.

Corrosion of Metals by Oil.

Experiments to determine the action of oils upon copper and iron plates ten square feet resulted, viz.:

All Pure Oils.	10-Days' Exposure on Copper. Gain in Weight. Grains.	24-Days' Exposure on Iron. Gain in Weight. Grains.
Almond.	0.103	0.0040
Colza.	0.017	0.08
Castor.	0.010	0.0048
Lard.	0.013	0.025
Linseed, raw.	0.30	0.005
Neat's-foot.	0.11	0.0875
Olive.	0.22	0.0062
Paraffin.	0.0015	0.0045
Seal.	0.0485	0.005
Sperm.	0.003	0.046

The result shows that the action of any oil upon any one metal is no guide to the degree that it will affect another metal, but that all metals are affected by oil to some degree. (W. H. Watson.)

In other experiments upon commercial linseed-oils made from unripe seeds by the steam and dioxide-of-carbon processes, also of sulphuric-acid cleared oils and petroleum oils containing traces of sulphur, the corrosive action was from two to three times the above amounts on both the copper and iron.

The corrosive effects of oils in contact with different metals at ordinary summer temperatures, are as follows:

Oils.	Metals Not Attacked.	Metals Least Attacked.	Metals Most Attacked.
Mineral.	Zinc and copper	Bronze	Lead
Olive.	" " "	Tin	Copper
Colza.	Bronze and tin	Iron	"
Tallow.	" " "	Tin	"
Lard.	" " "	Zinc	"
Cottonseed	" " "	Lead	Tin
Spermaceti.	" " "	Bronze	Zinc
Seal.	" " "	Bronze	Copper
Whale.	Tin	Bronze	Lead

ANALYSIS OF SAMPLES OF MELTED SNOW FROM A NUMBER OF LOCALITIES, SHOWING CORROSIVE INGREDIENTS. (PROF. VIVIAN B. LEWES, PH.D.)

Carbon (soot)	39.00	per cent	51.30 per cent inert.
Hydrocarbons	12.30	“ “	
Sulphuric acid	4.33	“ “	Corrosive, 7.03 per cent.
Hydrochloric acid	1.33	“ “	
Ammonia	1.37	“ “	
Metallic iron and black magnetic oxide	2.63	“ “	Metallic.
Mineral matter, chiefly silica and ferric oxide	31.24	“ “	Mineral.
Organic matter	1.20	“ “	7.80 per cent decomposable.
Loss and undetermined	6.60	“ “	
	100.00	“ “	

Corrosive Elements of Smoke and Fog.

The composition of smoke in the cities of London and Glasgow as analyzed by Mr. W. R. Hutton* also includes the soot deposited by the smoke after being diluted by the air under the conditions of an English foggy day.

Substance.	London.		Glasgow.	
Tar and oil	18.00%	Non-corrosive, 71.18%	15.00%	Non-corrosive substances, 50.70%
Carbon	53.18%		35.70%	
Sand	14.40%	Mineral and Metallic, 18.72%	25.70%	Mineral and Metallic, 27.80%
Iron	0.40%		0.70%	
Soda	0.34%		0.30%	
Lime	1.00%		0.80%	
Magnesia	0.30%		trace	
Potash	0.20%		0.30%	
Phosphates of lime and magnesia	2.08%		3.20%	
Sulphuric acid	4.60%	Corrosive elements, 10.10%	7.90%	Corrosive substances, 21.50%
Chlorine	trace		0.40%	
Sulphocyanogen	0.25%		none	
Carbonic acid	0.70%		trace	
Ammonia	1.75%		2.80%	
Water	2.80%		7.20%	
	100.00%	100.00%	100.00%	100.00%

Dr. W. G. Blake found that the dust and soot in the central district of Edinburgh in 1902, deposited in open vessels, amounted to 38 ounces per square foot, or about 24 pounds per year for every

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* "Chemistry of Coal Smoke." A paper read before the Chemical Section, Glasgow Philosophical Society, Glasgow, Scotland.

100 square feet of surface. It was highly charged with sulphuric acid, albuminous, vegetable, and animal substances as well as soot and cinders.

The Weight of Air, Vapor of Water, and Mixtures of Air and Vapor at Different Temperatures under the Ordinary Atmospheric Pressure of 29.921 Inches in the Barometer. (Thos. Box.)

Temperature, F.	Volume of Dry Air at Different Temperatures, the Volume at 32° F. being 1.000.	Weight of a Cubic Foot of Dry Air at Different Temperatures, in Pounds.	Elastic Force of Vapor, in Inches of Mercury (Regnault).	Elastic Force of the Air, in a Mixture of Air and Vapor, in Inches of Mercury.	Weight of a Cubic Foot of the Mixture of Air and Vapor.			Weight of the Vapor Mixed with 1 lb. of Air, in Pounds.	Weight of Dry Air Mixed with 1 lb. of Vapor.
					Weight of the Air, in Pounds Avoir.	Weight of the Vapor, in Pounds Avoir.	Total Weight, in Pounds Avoir.		
Degrees									Lbs.
32	1.000	.0807	.181	29.740	.0802	.000304	.080504	.00379	263.81
42	1.020	.0791	.267	29.654	.0784	.000440	.078840	.00561	178.18
52	1.041	.0776	.388	29.533	.0766	.000627	.077227	.00819	122.17
62	1.061	.0761	.556	29.365	.0747	.000881	.075581	.01179	84.79
72	1.082	.0747	.785	29.136	.0727	.001221	.073921	.01680	59.54
82	1.102	.0733	1.092	28.829	.0706	.001667	.072267	.02361	42.35
92	1.122	.0720	1.501	28.420	.0684	.002250	.070717	.03289	30.40
102	1.143	.0707	2.036	27.885	.0659	.002997	.068897	.04547	21.98
112	1.163	.0694	2.731	27.190	.0631	.003946	.067046	.06253	15.99
122	1.184	.0682	3.621	26.300	.0599	.005142	.065042	.08584	11.65
132	1.204	.0671	4.752	25.169	.0564	.006639	.063039	.11771	8.49
142	1.224	.0660	6.165	23.756	.0524	.008473	.060873	.16170	6.18
152	1.245	.0649	7.930	21.991	.0477	.010716	.058416	.22465	4.45
182	1.306	.0618	15.960	13.961	.0288	.020536	.049336	.71300	1.402
212	1.367	.0591	29.921	0.000	.0000	.036820	.036820	Infinite	00.00

VEHICLES AND SOLVENTS.

Substance.	Specific Gravity.	Pounds per Gallon.
Bisulphide of carbon, CS_2.	1.26	10.513
Tetrachloride of carbon, CCl_4.	1.56	13.00
Benzine, 62° B.	0.730	6.09
" 66° B.	0.712	5.94
Cotton-seed oil, crude.	0.9224	7.696
" " refined yellow.	0.9230	7.701
" " water-white.	0.9288	7.749
Cod-oil (tanners')	0.9205	7.686
Menhaden-oil, dark.	0.9292	7.741
" light.	0.9325	7.781
Porgy-oil.	0.9332	7.786
Poppy-seed oil.	0.9245	7.723
Linseed-oil, raw, pure.	0.9299	7.759
" boiled, pure	0.9411	7.853
Lucol (substitute for linseed-oil.)	0.8993	7.50
Resin-oil, third run.	0.9887	8.2497
" other runs.	0.9910	8.269
" " "	0.960	8.01
Petroleum, Lima, crude.	0.839	7.00
" other brands.	0.811	6.77
Turpentine-oil, pure ($C_{10}H_{16}$).	0.870	7.262
" commercial.	0.855	7.134
Water.	1.000	8.344
Other oils and fats, see page 418.		
Ammonia, 27.9 per cent.	0.91	7.59
Alcohol, pure.	0.794	6.625
" 95 per cent.	0.816	6.808
Acetic acid, hydrated ($C_2H_4O_3$).	1.10	9.178
Sulphuric acid (H_2OSO_3).	1.849	15.43
" " anhydrous (H_2SO_4)	1.97	16.438
Muriatic acid (Hydrochloric) } HCl or (H_2Cl_2)	1.2	10.020
Nitric acid (HNO_3)	1.52	12.710
Carbonic acid, CO_2.	1.524	12.716
" " gas.	0.11636=	8.594 cu. ft. per pound.
Glycerine, ($C_3H_8O_3$) Carbon, 40 per cent Hydrogen, 9 " " Oxygen 51 " "	1.261 to 1.27	10.597
Olein.	0.93	7.76

Substance.	Specific Gravity.	Remarks.
Acrolein, C_3H_4O.		Vegetable fatty-oil acids.
Acrolic acid, $C_3H_4O_2$.		
Acetic acid, $C_2H_4O_3$.	1.0635	
Margaric acid, $C_{17}H_{34}O_2$.	0.810	
Oleic acid, $C_{18}H_{34}O_2$.	0.808	
Oleic ether, $C_{20}H_{33}O_2$.	0.807	
(Dissolves all solid fats, stearic, palmitic, and other fatty acids.)		
Stearic acid, $C_{18}H_{36}O_2$.	0.805	
Palmitic or Benic acid, $C_{16}H_{32}O_2$.	0.803	
Glycerine ether, $C_3H_{12}O_3$		
Stearic acid, $C_{18}H_{36}O_2$.	1.01	
Stearic ether, $C_{19}H_{38}O_2$.	1.0	
Stearine, $C_{21}H_{42}O_4$.	0.9245	
Glycerine, $C_3H_8O_3$.	1.268	
Paraffin, $C_{27}H_{54}$ or $C_{27}H_{56}$	0.87	Melts at 112° to 149° F. Boils at 700° F.
= Carbon, 85.31 per cent. Hydrogen, 14.44 " "		
Fibrine:		
Vegetable, $C_{54.2}H_{7.5}N_{15.8}$.	1.2568	
Fish, $C_{54.7}H_{7.2}N_{15.4}S_{11.5}$.	1.2617	
Albumin:		
Animal, $C_{53.4}H_{7.1}N_{15.7}$.	1.2351	
Vegetable, $C_{54.3}H_{7.1}N_{15.8}$.	1.2412	
Bisulphide of carbon, CS_2.	1.072*	Boiling-point 109.4° to 118.4° F.
= Carbon, 15.8 per cent.	2.6296 to	
Sulphur, 84.2 " "	2.6447†	
Tetrachloride of carbon, CCl_4.	1.56	Boils at 170° F.; weight 13 pounds per gallon.
Linoleic acid, $C_{16}H_{26}O_2$.	0.953	
Oxylinoleic acid, $C_{16}H_{26}O_5$.	1.016	

* At 32° F. † At 60° F.

Proportions of Oil in Pigment Pastes.

It is often important to know the amount of oil necessary to form a paste with the different pigments. This amount necessarily varies, owing to the condition of some of the pigments before mixing and the fineness of grinding. The following is a general average of the percentage of oil in 100 pounds of commercial paste from pure pigments:

White lead, pure	8 to 9 per cent.
Red lead, pure	12 " "
Sublimed lead	10 " "
Zinc oxide or white, French	16 " "
" " " " American	18 " "
Whiting paste	20 " "
" putty	18 " "

China clay	23	per	cent.
Terra alba	22	"	"
Barytes	8 to 10	"	"
Silica, or silex, floated	25	"	"
Lampblack	65 to 70	"	"
Drop-black	50	"	"
Gas-black	80 to 84	"	"
Mineral black	35 to 40	"	"
Graphite	30 to 35	"	"
Mineral brown	22 to 25	"	"
Vandyke brown	45 to 50	"	"
Burnt Sienna, American	35	"	"
" " Italian	50	"	"
Raw Sienna, American	40	"	"
" " Italian	55	"	"
Burnt umber, Turkey	42 to 45	"	"
" " American	35	"	"
Raw umber, Turkey	40	"	"
" " American	35	"	"
French ochre	30 to 33	"	"
Yellow " American	28 to 30	"	"
Oxford " English	25 to 30	"	"
Indian red	20	"	"
Oxides of iron	23 to 25	"	"
Venetian red	23 to 25	"	"
Tuscan red	23 to 26	"	"
Rose pink	30 to 35	"	"
Carmine, French	50 to 54	"	"
Vermilion, American	20 to 22	"	"
" English	15 to 18	"	"
" artificial (according to the specific gravity of the pigment)	15 to 30	"	"
Chinese or Prussian blue	50	"	"
Ultramarine blue	30	"	"
Light chrome yellow	20	"	"
Medium chrome yellow	26	"	"
Dark or orange yellow	22	"	"
Chrome green, pure (according to the shade)	26 to 35	"	"
Chrome green, commercial (the lightest shades require the least oil	15 to 23	"	"
Yellow lake, French	38	"	"

Berzelius' series of electro-chemical elements and their symbols are as follows (those in italics are the pigment class):

Element.	Symbol.	Element.	Symbol.	Element.	Symbol.
Oxygen.	O	*Silicon.*	Si	*Manganese.*	Mn
Sulphur.	S	*Hydrogen.*	H	Uranium.	U
Silenium.	Se	Gold.	Au	Cerium.	Ce
Nitrogen.	N	Osmium.	Os	Thorium.	Th
Fluorine.	F	Indium.	Ir	Zirconium.	Zr
Chlorine.	Cl	Platinum.	Pt	*Aluminium.*	Al
Bromine.	Br	Rhodium.	R	Didymium.	D
Iodine.	I	Palladium.	Pd	Lanthanum.	La
Phosphorus.	P	*Mercury.*	Hg	Yttrium.	Y
Arsenic.	As	*Silver.*	Ag	Glucinum.	G
Vanadium.	V	*Copper.*	Cu	Magnesium.	Mg
Molybdenum.	Mo	*Bismuth.*	Bi	*Calcium.*	Ca
Tungsten.	W	*Tin.*	Sa	Strontium.	Sr
Boron.	B	*Lead.*	Pb	*Barium.*	Ba
Carbon.	C	Cadmium.	Cd	Lithium.	L
Antimony.	Sb	*Cobalt.*	Co	*Sodium.*	Na
Tellurium.	Te	*Nickel.*	Ni	*Potassium.*	K
Tantatum.	Ta	*Iron.*	Fe		
Titanium.	Ti	*Zinc.*	Zn		

Each metal is *electro-negative* to all that follow it in the list, and *electro-positive* to all that precede it, dilute sulphuric acid being the exciting liquid. Alloys of the metals vary the above order of location to a small extent, and all excitant acids also change the order slightly.

The amount of electro-chemical force developed in the oxidation of metallic *substances and their oxides* is given on pages 353, 354, 355.

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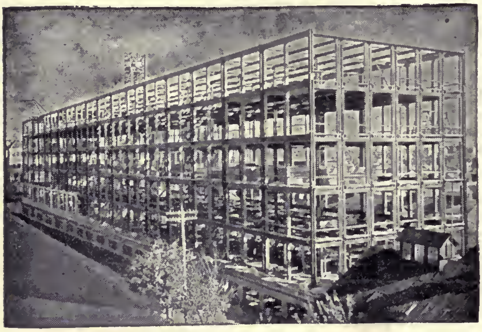

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