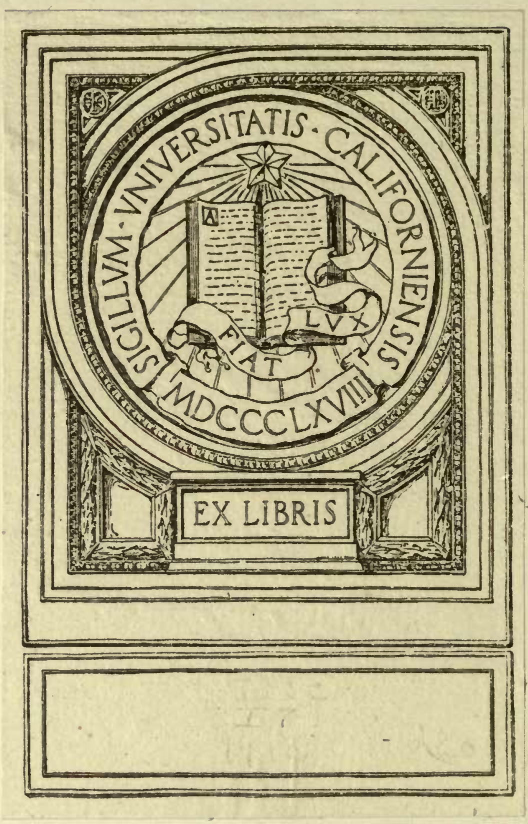
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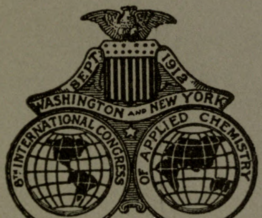
EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION IX
PHOTOCHEMISTRY



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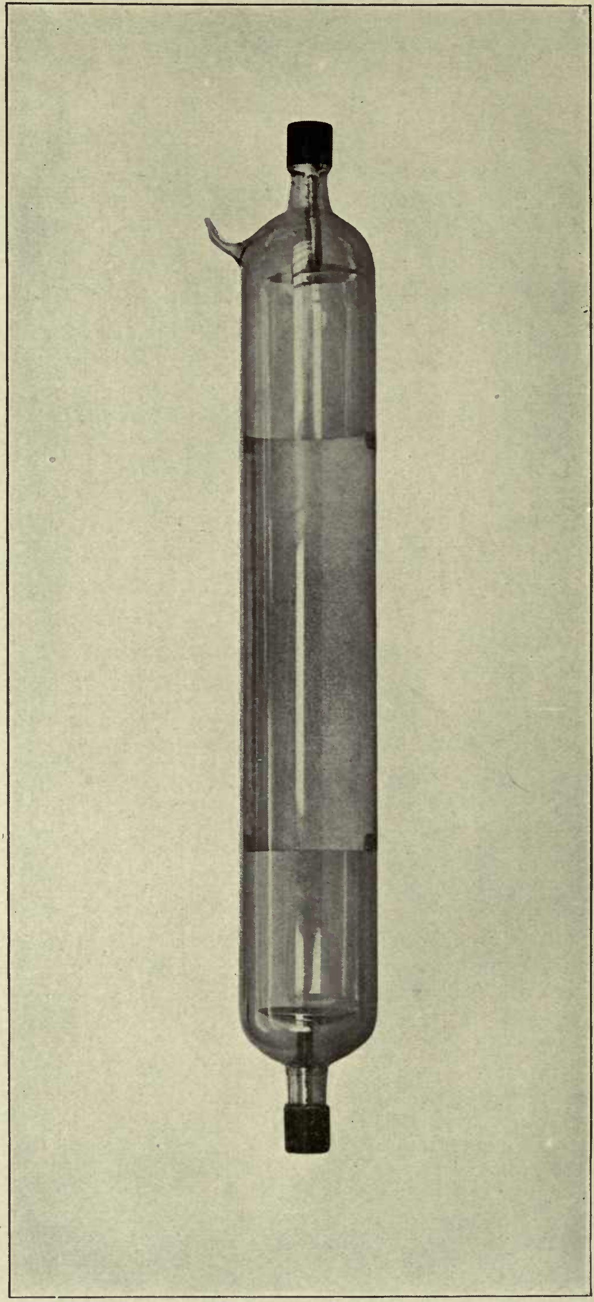


Vacuum Tube with Fluorescent Screen.

NOTES ON FLUORESCENCE AND PHOSPHORESCENCE

By W. S. Andrews
Schenectady, N. Y.

In the following notes only slight attempt has been made to discuss the above phenomena from an academic point of view, as this has already been done in various books and papers by more competent men. The writer has therefore preferred to confine his remarks chiefly to the results of experimental work pointing to possible utilitarian purposes.

The general term "Luminescence" has been applied to light which is independent of incandescent heat, and it is divided under numerous headings according to its nature and origin. One of these headings is Radio-luminescence, which applies to light that is emitted by certain substances under the stimulation of other light, or in some cases of electric radiations such as cathode rays, etc. Under this heading we find the transient effect known as Fluorescence which, if it persists after the exciting cause is cut off, is termed Phosphorescence.

It is conceded that strictly speaking, the term fluorescence applies only to liquids and gases, but in the present paper, although only solid bodies are considered, their fluorescent and phosphorescent colors are mentioned for the reason that in some cases the persistence of the luminescent effect is so transient that it can be hardly detected even in a phosphoroscope.

When a substance is exposed to a mixture of visible light and invisible ultra-violet radiation, as in the case of the unscreened iron arc, etc., the true luminescent color is manifestly more or less masked or changed by the visible reflected light, and the real color can only be seen in a phosphoroscope, or in cases of extremely transient phosphorescence, such as that shown by the salts of salicylic acid, in a spectrum, wherein the invisible ultra-violet rays are dispersed beyond the visible spectrum by a quartz prism.

With this explanation in mind, to say that a certain substance is fluorescent or phosphorescent, means that when it is properly stimulated it will emit light of a predominating color, irrespective of the frequencies of the incident waves by which it is excited, although in general, these incident waves must be of shorter length and therefore higher frequency than those of the predominating fluorescent light emitted. The incident waves need not be within the visible spectrum, for some of the brightest fluorescent effects are produced by the invisible waves of ultraviolet light.

The term "predominating color" is used because a fluorescent or phosphorescent color is usually compound, that is, it can be split up into a more or less continuous spectrum, a portion of which is usually more intense than the other parts, which gives a predominating color tone to the light when seen by the unaided eye. Certain compounds of cadmium, for example, exhibit a bright yellow or orange color, but when examined through a spectroscope a considerable amount of red, green and blue light is also seen.

It must be understood that these remarks apply only to phosphorescence as related to radio-luminescence. There are other kinds of similar phenomena, such as the chemi-phosphorescence of phosphorus, the biological or animal phosphorescence emitted by the glowworm and the firefly, etc., but as these and other examples are independent of light rays as an excitant, they are in a different class, and will not come under present consideration.

The atomic or electronic mechanism by which fluorescence and phosphorescence are produced is unknown, but the fact that it often appears in very dilute "solid solutions" suggests the possibility that the comparatively few atoms of the solvent are held in suspension in such a way that their motions, when energized by the ether waves which they absorb, are for the most part limited, or tuned to harmonize with the frequency of the light waves which produce the predominating colors. Fluorescence or phosphorescence of very short duration may be due to the vibrations being impeded, as a pendulum is when swinging in water, and when the phosphorescence is more or less persistent, the vibrations may be compared to the more sustained motion of a pendulum swinging in air or in a vacuum. It has also been suggested by Mendellèef that certain double salts are formed, which undergo decomposition and re-formation under the alternate influence of light and darkness, and the resulting changes in the disposition of the atoms are evidenced in light. These suggestions, however, are purely speculative, and it is generally admitted that there is no satisfactory hypothesis which will explain these phenomena intelligently. Furthermore, as pointed out by Wood,[1] the fluorescence or phosphorescence of a given substance appears to depend as much on its molecular condition as on its chemical constitution. For example, some of the aniline dyes, such as rhodamin and fluorescence, are strongly fluorescent when in liquid or solid solution, but are inert in this respect in their pure solid state, while other substances, such as barium platino-cyanide, are strongly fluorescent in their solid state, but lose this property when in solution. Also, compounds such as most of the sulphides require minute quantities of other substances to bring out their fluorescent and phosphorescent properties — while others again, such as calcium tungstate, show the best results when absolutely pure.

The first historical reference to phosphorescent material dates back to about the year 1602, when it is recorded that a shoemaker in Bologna discovered that some stones which he had made red-hot continued to emit light in the dark after they had cooled. At about this time also, a German chemist named Brandt discovered a method for making a crude kind of phosphorus from bones and other animal matter which also glowed in the dark, so it was thought that these two substances were in some way related to each other and for many years, thereafter, the material which the shoemaker had discovered was called "Bolonese Phosphorus." It is now well known that it was simply barium sulphate or heavy spar, found near the city where he lived, and which by calcination was partially converted into phosphorescent barium sulphide.

About the year 1769, the English chemist Canton discovered the same luminous property in calcium sulphide which, in accordance with the custom of those times, was termed "Canton's Phosphorus" in the old works on chemistry. These and many other phosphorescent compounds have excited the interest of scientists from the early days of their first discovery down to the

[1] "Physical Optics," by R. W. Wood, LL.D., 1911, p. 569.

present time, and they have been carefully investigated by many distinguished men too numerous to mention, but they appear to have attracted notice principally from a point of academic interest rather than from any idea of their practical application in the production of useful light.

Some time during the latter half of the last century, however, Professor Balmain, of the London University, devoted considerable time and skill to experiments along these lines, and he finally developed a method for making phosphorescent calcium sulphide which has found commercial applications and which has since been known as "Balmain's Luminous Paint." Professor Balmain died in 1877 and left the secret of his luminous preparation to his assistant, Mr. A. J. Horne, who is now living in Surrey, England. Mr. Horne still continues the business of making the paint, and he has succeeded in greatly improving its luminous intensity so that it is now used to a considerable extent in England and elsewhere for painting sign-posts, gates and gateposts, beacons along river banks and harbors, life buoys, pier heads and other objects which it is desirable to make visible in the dark for directive or warning purposes in the absence of other light.

Five of the metallic elements are remarkable for the fluorescent and phosphorescent properties shown by some of their compounds, and it is a noteworthy fact that these elements are found in *consecutive order* in the second group of Mendellèef's table of the Periodic Law as follows:

Calcium,	Atomic mass 40.1
Zinc,	Atomic mass 65.4
Strontium,	Atomic mass 87.5
Cadmium	Atomic mass 112.4
Barium,	Atomic mass 137.4

The sulphides of all the above-mentioned metals with the possible exception of cadmium are more or less phosphorescent and fluorescent, but in order to bring out this quality to the best advantage, they require to contain, in solid solution, a definite but exceedingly minute quantity of some other element.

Manganese, copper and bismuth are among the best of these so-called excitants and they are used in quantities of 1/1000th to

1/10,000th part, by weight, of the matrix. In order to facilitate their solution in the latter, a flux, usually consisting of some salt of potassium or sodium, has been found serviceable. The necessary amount of flux is variable with different bases, but is commonly 1/150th to 1/300th part, by weight, of the matrix.

The sulphide of a given base, such as calcium, can be made to exhibit different phosphorescent and fluorescent colors by changes in the exciting elements and the fluxes, and also by varying the period and temperature of calcination, probably owing to the occurrence of certain chemical reactions between the elements at definite high temperatures.

When electricity is passed through a vacuum tube a part of the energy is expended in the production of invisible radiation, and it is evident that the efficiency of the tube as a light producer is thereby decreased in proportion to the amount of energy thus expended. If a suitable fluorescent material is introduced into the tube, some of this invisible radiation will be transformed into visible light and its illuminating efficiency will be proportionally increased. Some of the materials to be described later have been found to work fairly well in this way but each one shows some predominating color such as red, yellow, green or blue, and is therefore unsuitable for general lighting purposes. If by combinations or in any other way, a white or nearly white fluorescence of good intensity can be produced, and providing the material used is sufficiently stable, it might be found serviceable for improving the illuminating efficiency, as above described. Furthermore, a fluorescent material of a definite color might be used to modify the spectrum of a tube containing a rarefied gas or vapor.

In the examination of numerous compounds five different sources of radiation have been utilized as follows:

The Mercury Arc, the light of which is rich in the extreme blue and violet rays of the visible spectrum and also in ultra-violet radiation. The glass tube which encloses the mercury arc being opaque to ultra-violet waves of the higher frequencies naturally limits the use of this light to a class of compounds which are excited to phosphorescence by the waves of lower frequencies.

The Iron Arc, produced by the disruptive oscillatory discharge of a condenser, between iron terminals, the condenser being connected to an A. C. circuit of 2500 to 10,000 volts. This arc radiates a considerable amount of ultra-violet light, and being unenclosed, its rays are only subject to the absorbtive influence of the surrounding air. A phosphoroscope with iron arc illumination has been found useful for the examination of short period phosphorescent substances.

The Vacuum Tube. Special tubes have been designed and made for this work, prints of which with description in detail are attached. In testing the preparations, 60 cycle alternating current from 2500 to 10,000 volts was used with tubes having a vacuum of about one mm. of mercury, and tubes exhausted to a higher vacuum were operated by an induction coil or a Tesla high frequency coil. In the first case, the preparations were exposed to the radiations present in the interior of the ordinary Geissler tube, and in the second case, to cathode rays, in each case the preparation being placed inside the exhausted tube.

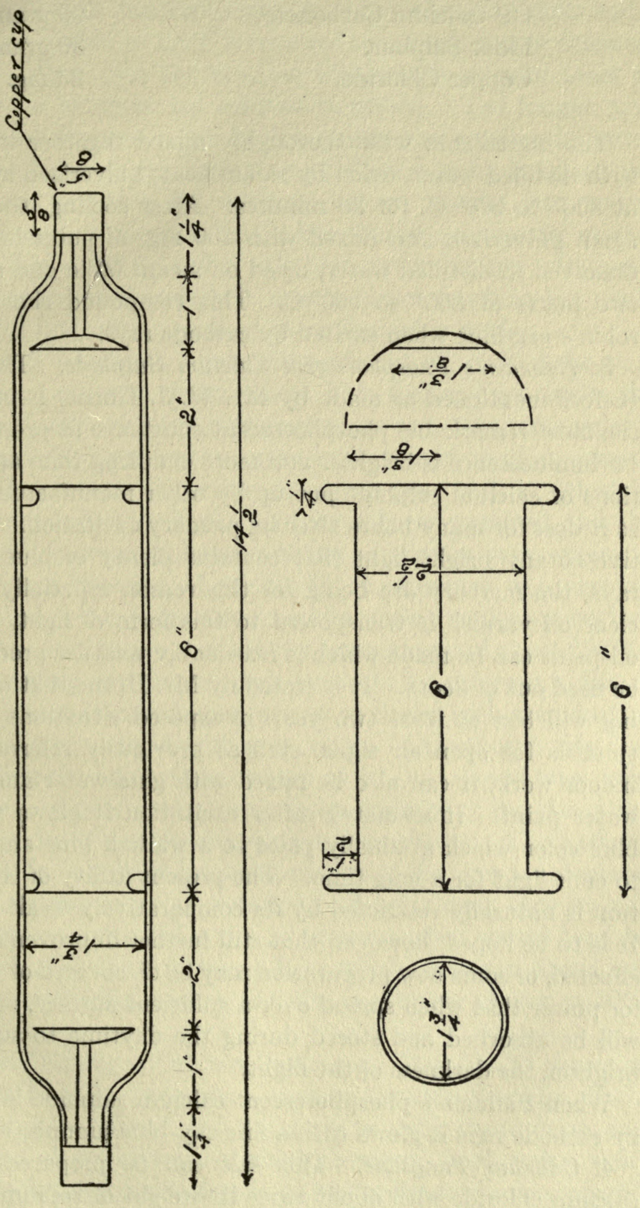
X-Rays. X-rays of moderate strength have also been used to test the various compounds.

Following is a brief description of seventeen different compounds, the behavior of which under each of the foregoing methods of excitation is given on separate sheet in tabulated form.

COMPOUNDS OF CALCIUM

1. *Calcined Calcium Sulphide.* Samples of CaS (marked cp) were obtained from Eimer & Amend, New York City, and Bausch & Lomb, Rochester, N. Y. The untreated samples showed a dull yellow P. & F. under the iron arc and in the vacuum tube, but after calcination for half an hour at 800° to 900° C. the color was much improved, showing to best advantage under cathode rays. These results indicate the presence of impurities in minute quantity, as it is probable that absolutely pure CaS exhibits no F. or P.

2. *Calcium Sulphide with Copper.* An endeavor was made to combine the above-mentioned samples of CaS with a minute quantity of copper, but the results were unsatisfactory. It is apparently necessary to incorporate the exciting element with the calcium base coincident with the change of the latter into its sulphide. The following mixture was therefore prepared:



EXPERIMENTAL VACUUM TUBE

CP Calcium Carbonate,	90 grams
Flour Sulphur,	30 grams
Copper Chloride,	25 mg.

The ingredients were thoroughly mixed together into a paste with distilled water, dried by steam heat; pulverized and calcined at 800° to 900° C. for 30 minutes. After cooling, the mass was again pulverized and mixed with 200 mg. of potassium sulphate dissolved in distilled water, dried on steam table and calcined for two hours at 800° to 900° C. This compound shows a bright robin's-egg blue when excited by cathode rays.

3. *Balmain's Phosphorescent Calcium Sulphide.* This material (before mentioned as made by Mr. W. J. Horne) is undoubtedly the most remarkable phosphorescent substance at present known. Its luminescence is brighter and more enduring than any preparations of calcium sulphide put up by other manufacturers, lasting as it does for many hours after its primary excitation. It is sensitive to any bright light that contains plenty of blue and violet rays, the mercury arc being for this reason especially good. As clear oil varnish is transparent to this form of light, a luminous oil-paint can be made which is reasonably weather proof, and may be used out of doors. It is stated by Mr. Horne that a good coating will last at least two years in exposed situations, making it suitable for open air signs, etc., as previously referred to. For indoor work, it can also be mixed with glue water and used as a water paint. Immediately after excitation it glows with a fine blue color which gradually pales to a whitish blue and continues to emit light for a long time. The present utility of this preparation is naturally restricted by its comparatively weak luminosity. It is to be hoped, however, that still further improvement may be effected, or some new preparation may be discovered of such superior power that when spread over a sufficient surface, enough light will be absorbed and stored during the daytime to substantially brighten the darkness of the night.

When Balmain's phosphorescent calcium sulphide is stimulated by cathode rays it glows with a fine sky-blue luminescence.

4. *Calcium Tungstate.* This salt can be prepared by fusing calcium chloride with about twice its weight of sodium tungstate.

Both salts must be chemically pure to obtain the best results and a temperature of 900° to 1000° is required to insure a proper chemical reaction. When cold the crucible will contain a hard mass of fused sodium chloride and calcium tungstate. The former may be gradually dissolved, but by immersing the crucible in water for several days, or the time may be shortened by breaking the crucible and crushing its contents before putting into water. Calcium tungstate shows a bright blue fluorescence under excitation of cathode rays — and a pale blue under X-rays. Its luminescence possesses considerable actinic power — which has made it useful for intensifying screens in radiographic work.

5. *Calcium Salicylate.* Salicylic acid and all of its salts thus far examined show a characteristic blue fluorescence under the excitation of ultra-violet rays from the iron arc. If these preparations have any phosphorescent property, it must be of an exceedingly short period as the writer has never been able to detect it. Many compounds of salicylic acid have been examined and the calcium salt appears to have a slight advantage over others in brightness and clearness of color. When examined in a vacuum tube, the blue color fades away rapidly, owing to decomposition, which occurs even in the open air at a temperature of about 220° C.

An interesting experiment may be made by painting a disc of black cardboard in radial lines, curves or circles with a mixture of calcium salicylate mixed with gum water. On rotating this disc and directing the light of an iron arc on it, the painted lines, etc., will fluoresce in synchronism with the periodicity of the disruptive discharge and produce pleasing stroboscopic effects. These effects may naturally be varied by manipulation of the iron terminals or by changing the speed of rotation. It is evident that in this experiment any appreciable phosphorescent effect would tend to blur the edges of the fluorescent lines which, however, stand out clearly and well defined when the disc is rotating as fast as 2000 r. p. m.

6. *Natural Calcite or Calcium Carbonate.* Pure $CaCO_3$ shows no appreciable F. or P., but certain samples found in Franklin, N. J., exhibit various shades of pink fluorescence under the iron arc, and a bright red phosphorescence, which, however, is of such a short duration with this stimulation as to be hardly noticeable, except-

ing when seen in the phosphoroscope. When excited by cathode rays in a vacuum tube the phosphorescence is more persistent, so that after the current is cut off the calcite continues to glow for some time like a red-hot coal.

COMPOUNDS OF ZINC

7. *Natural Willemite or Zinc Silicate.* Pure zinc silicate either natural or artificially prepared has no F. or P., but samples of willemite found in Franklin, N. J., show a brilliant green fluorescence, probably on account of their containing a minute quantity of manganese. By reference to the table it will be seen that the fluorescence of this mineral may be stimulated to almost the same brightness by the iron arc-vacuum tube, or X-rays.

8. *Artificial Zinc Silicate.* A compound containing zinc silicate may be prepared which exhibits the same green fluorescence as the natural mineral, but differs from it in the fact that while the latter has a brilliant fluorescence but a weak phosphorescence of short duration, the artificial product has not such a bright fluorescence but shows a much stronger and more persistent phosphorescence. This compound may be prepared as follows:

CP	Zinc Chloride,	100.0 grams
CP	Sodium Silicate (sp. gr. 405),	100.0 grams
CP	Manganese Sulphate,	.02 grams

The zinc chloride is dissolved in 200 cc. of distilled water, and about 100 cc. of water is added to the sodium silicate. The manganese sulphate is dissolved in sufficient water and stirred thoroughly into the zinc chloride solution. The two solutions are then mixed together in a mortar, triturated to a cream and dried by steam heat. When dry, the mass is pulverized and calcined at about 800° C. for two or three hours.

9. *Phosphorescent Zinc Sulphide* (*Sidot's Blende*). This is a French preparation ("sulfure de zinc") and it is remarkable in showing a brilliant light-green fluorescence under the influence of cathode rays. As it can be stimulated by visible light at the violet end of the spectrum, like phosphorescent calcium sulphide, it may be mixed with any clear oil varnish and used as an oil paint or it may be used as a water paint by mixing it with gum-water.

In either case if a piece of white cardboard is coated with the paint and exposed for a few moments to the mercury arc, on removal from the light it will continue to glow for some time with a fine green phosphorescence. If then a part of the painted surface is protected by a card and the other part is exposed to the rays of an ordinary incandescent ruby lamp, the phosphorescence of the surface thus exposed to the red rays will be almost extinguished, whereas the protected part of the card will continue to glow as brightly as ever. This simple experiment strikingly illustrates the damping effect of red light on the green phosphorescence. A similar experiment may be tried with Balmain's luminous paint but the latter is not as sensitive to red light as the zinc preparation, and the damping effect is not so evident.

10. *Calcined Zinc Sulphate.* To prepare this compound, dissolve separately 100 grams of zinc sulphate and one gram of manganese sulphate in distilled water, mix the solutions and stir well together, then filter and evaporate to dryness on a steam table. The resulting dry crystalline mass must be pulverized and then calcined at not over 900° C. for two or three hours. If the temperature rises to 950° or 1000° C. the mass will turn brown and be useless. When properly made this compound shows a red fluorescence under the iron arc or cathode rays and also a fine dark-red phosphorescence of considerable persistency, looking like a bed of red-hot material. It is well known that zinc sulphate becomes anhydrous at 400° C. and is decomposed into $ZnO-$, O_2 and SO_2 at higher temperatures so it is probable that the above preparation consists largely of ZnO holding MnO in solid solution. It will be noted that two of the above preparations of zinc show green, and the third red fluorescence and phosphorescence, the variations in color given by this base, under different treatments, being as strongly contrasted as they are in preparations of calcium.

COMPOUNDS OF STRONTIUM

11. *Strontium Sulphide.* A sample of the above (marked cp) was procured from Bausch & Lomb, which showed a weak green phosphorescence.

Calcination for two hours at about 900° C. effected a marked improvement in color and persistency. After exposure to the mercury arc, it phosphoresced a bright yellowish green and under cathode rays it showed the same color.

12. *Strontium Sulphide with Copper.* A preparation was made by dissolving 10 mg. of copper chloride in absolute alcohol and thoroughly incorporating the solution with 10 grams of the above SrS. When dry, the mixture was calcined at about 900° C. for 30 minutes. Excepting that its former green phosphorescence showed a slight bluish tone, no apparent change resulted from this treatment.

COMPOUNDS OF CADMIUM

13. *Calcined Cadmium Sulphate.* Anhydrous cadmium sulphate made by calcining the hydrated salt at a low red heat shows a weak red fluorescence under the iron arc, and phosphoresces a faint yellow, probably on account of impurities in such minute quantity as to be difficult to detect by ordinary analysis. The characteristic bright yellow F. & P. of this element may be strongly developed by the addition of a small quantity of a manganese salt. To prepare this compound, dissolve 1000 parts by weight of cadmium sulphate in sufficient distilled water and add ten parts of manganese sulphate separately dissolved. Stir well together, filter, dry on steam table, pulverize and calcine at 800 to 900° C. for one hour. After this treatment it shows a bright primrose yellow F. and P. under the iron arc and cathode rays. X-rays also produce a yellow fluorescence but no appreciable phosphorescence.

14. *Cadmium Silicate.* A compound containing the above salt of cadmium may be thus made: Dissolve separately in distilled water 100 grams of cadmium chloride and 200 mg. of man. sulphate; mix the solutions and stir well together. Dilute 100 grams of liquid sodium silicate (sp. gr. 1.405) with an equal weight of distilled water. Add the cadmium solution and triturate in a mortar to a thin paste. Dry on a steam table, pulverize, and calcine at 900° C. for 30 minutes. This preparation shows a bright orange F. and P. under excitation similar to that mentioned in the last paragraph.

COMPOUNDS OF BARIUM

15. *Barium Sulphide.* This preparation may be made by intimately mixing 90 grams of cp. barium carbonate with 30 grams of

flour sulphur and then adding 25 mg. of copper chloride dissolved in sufficient distilled water to make the mixture into a thin paste. This paste must be dried on a steam table and calcined at about 800° C. for 30 minutes. When cold, the mass is pulverized and mixed with 200 mg. of potassium sulphate dissolved in enough water to form a paste, again dried and calcined at 800 to 1000° C. for about two hours. The compound thus made shows a golden yellow phosphorescence after exposure to the mercury arc.

16. *Barium Platino-cyanide.* This commercial compound of barium is extensively used for fluoroscope screens, on account of its brilliant fluorescence when excited by X-rays. It suffers, however, a gradual deterioration when thus used, slowly losing its fine green color which changes to a dull yellow, which is probably caused by its becoming partially dehydrated. The above-mentioned change takes place almost instantly in a rarefied atmosphere. If a small quantity of the salt is placed in a closed glass tube and connected with an air pump, on exhausting the air, its color will be seen to fade rapidly to a dull yellow. If the electric current is passed through the tube, the yellow will deepen to a brick-red, in which condition it will then show the characteristic yellow fluorescence of the barium compounds. The fresh salt shows a brilliant green fluorescence under the iron arc but it has no appreciable phosphorescence.

URANIUM FLUORIDE

17. This compound of uranium exhibits a bright-green fluorescence when excited by X-rays, and it is therefore sometimes used for fluoroscope screens which may be made by mixing it with weak gum-water and painting over white cardboard. It may be prepared as follows: Dissolve separately 10 grams of uranyl nitrate in 40 cc. of distilled water and 15 grams of ammonium fluoride in the smallest possible amount of water that will take it up. Mix the two solutions, collect the precipitate on a filter and dry without washing. If a glass beaker is used when dissolving the ammonium fluoride it must naturally be protected inside with a coating of paraffin or beeswax, as the solution would otherwise attack the glass.

EXPERIMENTAL VACUUM TUBES FOR SHOWING THE FLUORESCENT PROPERTIES OF DIFFERENT COMPOUNDS

Many experiments were made with different sizes and shapes of vacuum tubes and different forms of electrodes in order to find out how the fluorescent compound could be applied to the best advantage. The tube shown in Fig. 1 has been adopted for the present as a standard experimental pattern, the dimensions being given on the print.

The electrodes are made of sheet aluminum .025 in. thick and 1⅜ diameter, cup shaped with a radius of 1⅜ in. They are polished bright on both sides and riveted in the center to a piece of aluminum wire ⅛ in. diameter and 1½ in. long. A slot is cut in the other end of the aluminum wire and a short length of small platinum wire secured therein by compression, for sealing through the glass tube. Copper caps are fastened on the ends of the tubes with plaster of paris in the usual way and a copper wire extension of the platinum is soldered to the cap, thus providing strong and convenient terminals.

For applying the fluorescent materials to the inside of the tubes, sheet aluminum .025 in. thick is cut out to the shape and dimensions shown in Fig. 2, and then formed to fit the inside circumference of the glass tube — the diameter of the latter being about 1¾ in. The aluminum plates thus cover about one-half of the inside circumference of the tube, and the short projections serve as light springs to keep it in place. After the plates are made, they are roughened in weak hydrochloric acid to assist the adhesion of the powdered fluorescent material. A thin solution of water glass (sp. gr. 1.1) has been found to be the only practical adhesive material, as all kinds of resin or gum in solution will carbonise and are otherwise objectionable. Even water glass cannot be used with some compounds, as they are decomposed by it and lose their fluorescent properties. No better substitute, however, has been hitherto discovered.

In applying the compounds, the inner surface of the curved aluminum plate is first painted with the solution of water-glass, using a camel's-hair brush, and being careful to rub it on well, so as to thoroughly moisten every part of the surface to be covered.

The powdered compound is then applied with a fine sieve, the loose powder shaken off, and the plates left to dry slowly in the air. This process has been found satisfactory for most of the compounds used — especially so for those which are insoluble in water.

CONCLUSIONS

From a study of the phenomena briefly described in the foregoing pages there appear to be at present two special lines of research in this connection which may lead to practical and useful results, viz:

First. To improve the brightness and persistency of phosphorescence in calcium sulphide, or to discover some other compound giving better results.

Second. To find good fluorescent compounds for use in vacuum tubes and the best method for applying the same, for increasing their luminous efficiency.

SYNOPSIS OF TESTS ON VARIOUS COMPOUNDS FOR FLUORESCENCE AND PHOSPHORESCENCE

Metals	Compounds Examined	Mercury Arc		Iron Arc		Vacuum Tube		Cathode Rays		X-Rays	
		F	P	F	P	F	P	F	P	F	P
Calcium	1 Calcined CaS	Ft. yel.	None	Br. yel.	Yellow	None	None	Br. yellow	Yellow	Dull yeilow	None
	2 Phost. CaS	Lt. blue	Ft. blue	Lt. blue	Ft. blue	Light blue	Ft. blue	Br. lt. blue	Ft. blue	Dull gr. blue	Ft. green
	3 Horne's CaS (Balmain's Lum. Pt.)	None	Br. blue persis't	Lt. blue	Violet persis't	None	Vt. per.	Br. blue	Vt. per.	Weak lt. blue	Ft. blue
	4 Calcium Tungstate	None	None	Lt. blue	Ft. blue	Lt. blue	Ft. blue	Br. blue	Ft. blue	Lt. blue	None
	5 Cal. Salicylate	None	None	Lt. blue	None	Lt. blue fades qck.	None	Lt. blue fades quickly	None	Very faint	None
	6 Cal. Carb. (Calcite)	None	None	Pink	Br. red	None	None	Red	Dr. red	Very ft. red	None
Zinc	7 Natural Zinc Silicate	None	None	Br. green	Ft. gr.	Br. green	Ft. green	Brilliant gr.	Ft. gr.	Br. green	Very faint
	8 Artificial Zinc Silicate	None	None	Green	Green	Green	Green	Br. green	Green	Green	Ft. green
	9 Phost. Zinc Sulphide	None	Br. green persis	Green	Gr. pers.	Brilliant green	Gr. per.	Brilliant green	Green per.	Br. green	Ft. green
	10 Calcined Zinc Sulphate	None	None	Pink	Dr. red	None	None	Br. red	Dr. red	Red	None
Stront.	11 Calcined Stron. Sulphide (Sr_3)	None	Gr. yel. persis	Green	Gr. per.	None	Ft. green	Lt. yel. gr.	Lt. gr. per.	Lt. green	Very faint
	12 Calcined Stron. Sulphide (Sr_5)	None	Bl. yel. persis	Lt. gr.	Lt. gr. persis	None	Ft. green	Br. lt. gr.	Lt. gr. per.	Lt. green	Faint
Cadmium	13 Calcined Cad. Sulphate	None	None	Br. yel.	Yellow	Br. yel.	Yellow	Br. yellow	Yellow	Dull yellow	None
	14 Cad. Silicate	None	None	Orange	Orange	Orange	Orange	Orange	Orange	Dull orange	None
Barium	15 Barium Platino-cyanide	Br. green	None	Br. gr.	None	Dull[1] Or.	None	Br. orange	None	Brilliant gr.	None
	16 Barium Sulphide	None	Gold yel. persis	Dull yel.	Yellow	Slight	Orange	Ft. orange	Orange	Ft. yellow	Faint
Uranium	17 Uranium Fluoride	Lt. gr.	None	Br. yel. green	None	Green	None	Green	None	Green	None

[1] Decomposes in vacuum.

CHEMILUMINESCENCE

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Since there is no known way of converting monochromatic light of one wave-length directly into monochromatic light of another wave-length, it follows that we must have some chemical action taking place whenever luminescence of any wave-length is produced by the action of light of another wave-length. Consequently, all cases of fluorescence and phosphorescence[1] are due to chemical action, and one of the problems of the chemist is to find out what the actual reactions are in each particular case. Some experiments along this line have already been made in my laboratory[2] and others are now in progress. It has been shown that cathode rays excite sodium chloride to a bluish luminescence and that this same luminescence can be obtained also by combustion of sodium or by placing sodium chloride at the extreme inner surface of the oxidizing zone of the Bunsen flame. We can get the yellow luminescence by the rapid combustion of sodium, by placing sodium chloride in the oxidizing zone of the Bunsen flame, or by the action of canal rays on sodium chloride. There seems to be no reason, experimental or theoretical, for making any fundamental distinction between flame spectra, spectra obtained by any form of electrical discharge, spectra obtained by direct chemical synthesis or decomposition, or spectra obtained by the action of light. If we except the so-called temperature radiation of solids, we are certainly safe in making the generalization that all other forms of luminescence are due to chemical reaction.

Personally, I am not inclined to make an exception of the so-called temperature radiation of solids. It would not surprise me in the least to find that this luminescence was due to the giving off or the taking up of electrons. As there is no satisfactory experi-

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[1] Cf. Wiedemann and Schmidt; Wied. Ann. *54*, 604; *56*, 201 (1895).

[2] Wilkinson: Jour. Phys. Chem. *13*, 703 (1909); Miss Stevenson: Ibid. *16*, 845 (1912).

mental evidence of this as yet, it will be safer to postpone discussion of this until some other time.

The generalization that luminescence is always due to chemical reaction is not new. Pringsheim[1] has made a very strong case for the view that no gas emits light except as a result of chemical action. Armstrong[2] has put forward the view that luminosity and line spectra are the expression—visible signs—of the changes attending the formation of molecules from their atoms, or, speaking generally, that they are consequences of chemical changes. The difficulty is that the generalization has not been taken seriously by anybody, not even by Pringsheim himself. People speak of the carbon spectrum, the cyanogen spectrum, and the carbon monoxide spectrum for instance, instead of speaking of the spectrum due to this, that, or the other reaction. There has been very little progress in the twenty years since Pringsheim's paper appeared.[3] This is not very surprising. People studied electromotive forces for a great many years before it became clear to them that we ought to speak of the electromotive force of a reaction[4] instead of the electromotive force of certain substances.

Having decided that luminescence is due to a chemical reaction, using the word reaction in the broadest sense, the next question is what reactions give out light and under what conditions. All reactions tend to emit light, and all reactions do emit light when the reaction velocity is sufficiently high, though the absolute speeds necessary in any two cases may be very different. This is merely a further extension of the results[5] previously obtained. Trautz points out that an extraordinary number of chemical reactions are accompanied by emission of light and that the intensity of light increases with increasing reaction velocity. It is easy to show that some reactions emit no visible light under certain conditions but do emit light when the conditions are more favorable. Wilkinson[6] found that "bismuth, tin, zinc, and cadmium all give negative results when heated in a current of oxygen. However, when cad-

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[1] Wied. Ann. *45*, 429 (1892).

[2] Proc. Roy. Soc. *70*, 99 (1902).

[3] Cf. however, J. J. Thomson: Chem. News, *103*, 265 (1911).

[4] Haber: Zeit. Elektrochemie, *7*, 443 (1901).

[5] Trautz: Zeit. phys. Chem. *53*, 1 (1905); Zeit. Elektrochemie, *14*, 453 (1908).

[6] Jour. Phys. Chem. *13*, 704 (1909).

mium is heated with a blast lamp until it volatilizes, it combines with oxygen and burns with a deep yellow flame to the reddish brown oxide. Zinc heated in the blast to boiling burns with a green flame." Cases of this sort could be duplicated indefinitely.

Bandrowski[1] says: "I first studied the crystallization of sodium chloride, potassium chloride, potassium bromide, potassium sulphate, and potassium nitrate from aqueous solutions. I caused the crystallization to take place under all sorts of conditions: at different temperatures; by evaporating on the water bath, on the sand bath, or over a free flame; by sudden cooling (passing the supersaturated solution through a spiral tube which was kept very cold). In no case was I able to detect any emission of light.

"I accounted for this negative result by assuming that, under these conditions, the ions combined so slowly and over so large a space that the emission of light was too faint to be detected by the eye, more especially since a very intense light was scarcely to be expected even under the most favorable conditions. It became necessary, therefore, to do the experiments under such conditions that the forcing back of the dissociation would be practically instantaneous. It seemed to me that this could be done by adding a liquid which would be miscible in all proportions with water but which would precipitate these salts. Alcohol and aqueous hydrochloric acid are such liquids.

"The experiment confirmed my assumption and I was able to obtain light effects which were fairly strong with some of the salts provided the concentrations of the two liquids were adjusted carefully."

Miss Stevenson[2] found that there was no visible light emitted when quinine sulphate was dehydrated slowly and that a photographic plate was not fogged by a month's exposure to slowly dehydrating quinine sulphate. Visible light is emitted if the dehydration takes place rapidly. There was a possibility that the wave-length of the light emitted during dehydration might be different when the dehydration was slow from that which was emitted when dehydration was rapid. If that were so, there should be a gradual change in the quality of the light if sulphuric acid,

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[1] Zeit. phys. Chem. *15*, 324 (1894).
[2] Jour. Phys. Chem. *15*, 854 (1911).

containing varying amounts, were added to the hydrated salt. This experiment was tried by Miss Stevenson. "The intensity of the light diminished as sulphuric acid, containing more and more water, was added to separate portions of hydrated quinine sulphate. No change in the color of the light could be detected. Moreover, the experiments of Nichols and Merritt,[1] who found that, with varying wave-length of exciting light, there was no change in the position of the wave-length of maximum density of fluorescent light, make a shifting of the wave-length of the light given off by quinine sulphate less probable."

These experiments of Miss Stevenson are only qualitative and merely make it probable that the variation with varying speed of dehydration is solely in the intensity of the light. We have other evidence that the composition of the light emitted by any given reaction is practically constant. Pringsheim[2] says that in the case of all the non-luminous (faintly luminous) flames, in which the combustion products are chiefly carbon dioxide and water, the radiation seems to depend only on the chemical reaction. The radiation of all these flames seems to be independent of the temperature and to be the same qualitatively[3] and quantitatively[4] when the same amounts of water and carbon dioxide are formed. Fredenhagen[5] confirms this, for he finds that in the whole field of the water vapor spectrum, the ordinary hydrogen flame and the oxyhydrogen flame emit practically the same amounts of energy, when referred to equal quantities of water, in spite of the fact that the temperature of the oxyhydrogen flame is approximately double that of the ordinary hydrogen flame.

In the case of the so-called temperature radiation from solids, the quality of the light changes with rising temperature. On the other hand, the change of the intensity with the temperature is described by a general formula applicable to all wave-lengths. If we omit this case, as before, we seem to be justified in concluding that a fairly definite spectrum corresponds to each definite re-

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[1] Phys. Rev. *19*, 18 (1904).

[2] Wied. Ann. *45*, 428 (1892).

[3] W. H. Julius: Arch. neerl. *22*, 310 (1888).

[4] R. V. Helmholtz: Die Licht- und Wärmestrahlung verbrennender Gase, 69 (1890).

[5] Zeit. Elektrochemie, *14*, 458 (1908.)

action and that any marked change in a spectrum indicates the occurrence of another reaction.

It is well known that the phosphorescent sulphides of zinc, calcium, strontium and barium do not phosphoresce unless they contain traces of copper, bismuth, manganese, etc., and it is also well known that the color of the light emitted by the phosphorescing sulphides seems to be determined by the nature and amount of the salts of copper, bismuth, manganese, etc., Wilkinson[1] found that the sulphates of sodium, lithium, potassium and zinc increase the phosphorescence of cadmium sulphate when exposed to cathode rays; but apparently without changing the quality of the emitted light to any appreciable extent. I interpret this to mean that these salts act as catalytic agents, accelerating the rate of reaction between cadmium oxide and sulphur trioxide, and thereby causing the emission of more light. In the case of the phosphorescent sulphides, the reaction which emits light must be a reaction of the salts of copper, bismuth, manganese, etc., while the sulphides of zinc, calcium, strontium or barium, act as a medium to permit dissociation just as water does with salts.

The general results of this paper are:

1. With the possible exception of the so-called temperature radiation from solids, luminescence is always due to a chemical reaction.

2. All reactions tend to emit light, and all reactions do emit light if the reaction velocity is sufficiently high.

3. The critical reaction velocity, necessary to the emission of light visible to the eye, may be very different with two different reactions.

4. The intensity of the emitted light increases with increasing reaction velocity.

5. The quality of the emitted light varies but slightly with the reaction velocity.

6. The sulphates of sodium, lithium, potassium, zinc, etc., increase the phosphorescence of cadmium sulphate under the cathode rays chiefly by increasing the rate at which cadmium oxide and sulphur trioxide combine.

7. In the case of the phosphorescent sulphides of zinc, calcium,

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[1] Jour. Phys. Chem. *13*, 719 (1909).

strontium and barium, the reaction which emits light is one involving the so-called impurities—the salts of copper, bismuth or manganese for instance.

8. It is possible that the so-called temperature radiation from solids may be due to a reaction involving electrons.

THE CHEMICAL ACTION OF LIGHT

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In 1818 Grotthuss formulated two laws of photochemistry:

I. Only those rays of light which are absorbed produce chemical action.

II. The action of a ray of light is analogous to that of a voltaic cell.

The first law is usually attributed to Draper and is universally accepted. In a series of papers[1] I have shown the usefulness of the second law as a working hypothesis. The time has now come when both of these laws can be worded more broadly. The general understanding of the first law is that only those rays of light which are absorbed cause chemical action; but that all of the absorbed rays are not necessarily active. I am inclined to doubt the accuracy of this last clause. I propose to word the first law as follows: All radiations tend to decompose the substances which absorb them[2]. Whether any measurable change takes place depends upon other conditions. With some silver salts or with Eder's solution of mercuric oxalate, we get visible decomposition. With chromium salts we get no measurable change unless some reducing agent is present. With some substances, the action of light causes fluorescence or phosphorescence, thus indicating the occurrence of chemical changes even though there may be no appreciable decomposition. With a copper sulphate solution there is no apparent effect due to light and yet it is certain that the difference in the light-sensitiveness of a copper sulphate and a silver sulphate solution is merely a difference in the strength of the depolarizer needed. By using the word radiations instead of light I am able to include cathode rays, etc., which some people might object to classifying as light.

While the statement that light acts as a voltaic cell has proved

[1] Bancroft: Jour. Phys. Chem. *12*, 209, 318, 417 (1908); *13*, 1,181, 269, 449, 538 (1909); *14*, 292 (1910).

[2] Bancroft: Jour. Am. Chem. Soc. *33*, 92 (1911).

to be an excellent working hypothesis for cases involving oxidation and reduction, its usefulness is not so striking in cases involving allotropic modifications or polymerization. It is true that Berthelot[1] has shown that soluble sulphur can be obtained at the anode by electrolyzing a solution of hydrogen sulphide and that insoluble sulphur can be obtained at the cathode by electrolyzing a solution of sulphuric or sulphurous acid; but the light is acting on sulphur and not on hydrogen sulphide or sulphurous acid. This did not bother me seriously at one time; but I then expected to prepare dianthracene electrolytically.[2] This has been tried and we have not been successful. As that was admittedly a crucial test, I am prepared to abide by the result. It is also not absolutely satisfactory to have to say, in the case of organic substances, that light produces the same decomposition products that we should get if we could electrolyze the substance in question. It is quite possible that these difficulties may be overcome and that somebody may prepare dianthracene electrolytically.

There is another more serious objection to the Grotthuss generalization in its present form. The selective action of light is much more marked than the selective action of the current. We can take a solution containing cadmium and copper sulphates and we can precipitate metallic copper by regulating the voltage. We cannot, however, precipitate cadmium from that solution before the copper, though we can do it if we change to a cyanide solution. Suppose that we have two dyes of different colors which are oxidized about equally readily. By changing the wave-length of the light we can cause one dye or the other to oxidize in the air. So far as I know the only analogy to this in electrochemistry is the reduction of nitrates and nitrites.[3] At a smooth platinum cathode nitrite is reduced more readily than nitrate while the reverse is true at a spongy copper cathode. One difference between light and the electric current is that the current is a single reagent except in so far as the specific nature of the electrode may make a difference, while light is a mixture of reagents. Light of one wave-length may act on one substance and

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[1] Ann. Chim. Phys. (3) *49*, 448 (1857).
[2] Trans. Am. Electrochem. Soc. *13*, 257 (1908).
[3] Müller and Spitzer: Zeit. Electrochemie, *11*, 509 (1905).

light of another wave-length on another, or lights of different wave-lengths may cause the same substance to react in different ways. This is not covered by the Grotthuss formulation and it is therefore necessary to make a more general statement.

I propose the following generalization as an improvement on the two laws of Grotthuss:

All radiations which are absorbed by a substance tend to eliminate that substance. It is entirely a question of chemistry whether any reaction takes place or what the reaction products are.

This is precisely analogous to the formulation which I have given[1] for electrolysis. "In the case of electrolysis the only specific action which we have to attribute to the current is that it tends to set free the anions at the anode and the cations at the cathode. What happens over and above that is a question of chemistry, depending on the reaction velocity and equilibrium relations in each particular case."

The formulation which I have given for the action of light covers the cases of oxidation and reduction as well as does the formulation of Grotthuss. What I wrote four years ago[2], is equally applicable today: "The chemical effect of the light is merely to eliminate, if possible, the substance absorbing the light. Whether that elimination takes place as a result of oxidation or of reduction is a matter which is quite independent of the light and which depends on the nature of the depolarizer. If the depolarizer is a sufficiently strong reducing agent, we get reduction by light. If the depolarizer is a sufficiently strong oxidizing agent, we get oxidation by light. If it is not sufficiently one or the other, we get no action by light. A very good instance of the variable action of light is to be found in the case of mercurous chloride. In the presence of a sufficiently powerful reducing agent, light reduces mercurous chloride to metallic mercury. In the presence of a sufficiently powerful oxidizing agent, light oxidizes mercurous chloride to a mercuric salt. If there is no more suitable depolarizer the mercurous chloride itself acts as a depolarizer and is changed to mercury and mercuric chloride."

When we come to the case of oxygen, we now find plain sailing.

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[1] Bancroft: Trans. Am. Electrochem. Soc. *8*, 33 (1905).

[2] Bancroft: Trans. Am. Electrochem. Soc. *13*, 246 (1908).

Light which is absorbed by oxygen tends to eliminate it, and we get the formation of ozone or of ions as the case may be. Light which is absorbed by ozone tends to convert it back into oxygen. In this case we get light accelerating both reactions. It is easy to see, however, that we might have a case where the displacement of equilibrium by light might be small and the light might apparently have very little effect on one modification, under the conditions of the experiment. This seems to be true with phosphorus. Ultra-violet light converts white phosphorus into red phosphorus but we know of no photochemical change of red phosphorus into white phosphorus. Such a change must take place at some temperature and with some wave-length of light. Here is where we are hampered by experimental limitations. I know of no satisfactory way of obtaining approximately monochromatic ultra-violet light of any given wave-length and of high intensity. The amount of ozone obtained by the silent discharge is the difference between the amount formed by waves shorter than 300 $\mu\mu$ and that decomposed by waves longer than 300 $\mu\mu$. If the chemical action of the waves longer than 300 $\mu\mu$ had been somewhat more vigorous or that of the shorter waves somewhat less vigorous, we should not get any ozone by means of the silent discharge even though ozone could still be made readily if the wave-lengths above 300 $\mu\mu$ could be cut off. When we get a suitable way of getting ultra-violet of any desired wave-length, we shall unquestionably be able to demonstrate the photochemical conversion of red phosphorus into white phosphorus, of insoluble sulphur into soluble sulphur, and of dianthracene into anthracene. The photochemical change of soluble sulphur into insoluble sulphur and of anthracene into dianthracene is covered by the formulation, which also foresees the possibility of certain rays causing anthracene to fluoresce[1] while others change it into dianthracene.

The formulation which I have given calls for the photochemical preparation of white phosphorus, which is not known, while the formulation by Grotthuss calls for the electrolytic production of dianthracene, which is not known. It might be asked whether we are any better off under the new régime than under the old one.

[1] Cf. Miss Stevenson: Jour. Phys. Chem. *15*, 845 (1911).

I think we are, because we are not bothered by hypothetical electrolysis in non-conducting systems, because we are not bothered by the selective action of light, and because it is open to us temporarily to believe that the photochemical conversion of red phosphorus has never been observed owing to its never having been looked for.

The results of this paper may be summed up as follows:

1. It is correct to say that only those rays which are absorbed produce chemical action; but it is incorrect to add that some absorbed rays have no tendency to produce chemical action.

2. The statement that light acts like a voltaic cell is not adequate to account for all the facts, though it has proved an admirable working hypothesis up to a certain point.

3. The most satisfactory formulation of the chemical action of light is that all radiations which are absorbed by a substance tend to eliminate that substance. It is a question of chemistry whether any reaction takes place and what the reaction products are.

4. Different radiations may cause the same substance to react in different ways.

THE DOUBLE SPECTRUM OF SODIUM CHLORIDE

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Wilkinson[1] found that a bluish light was emitted when sodium burned slowly in chlorine or oxygen, while the yellow flame, usually considered characteristic of sodium, was obtained when the combustion took place rapidly. Both the bluish and the yellow luminescence are evidently due to the sodium because they are modified but slightly by the nature of the acid radical, though Wilkinson noticed a trace of green in the flame when sodium burned in iodine. This point will be considered later. The problem for the chemist is to determine what the reactions are which give rise to the two spectra. One method of attacking the problem is to find out under what conditions these two spectra are obtained.

When canal rays act on sodium chloride we get the yellow luminescence[2], while cathode rays cause the bluish luminescence. Lenard[3] has shown that fused salts of the alkalies are luminescent, the sodium salts emitting a sky-blue light. This being so, one would expect to get a similar spectrum developed somewhere in the Bunsen flame and this has actually been observed by Lenard in that portion of the flame separating the reducing zone from the oxidizing zone. Lenard also showed that the yellow flame is electrically neutral while the bluish flame contains ions of some sort.

Bandrowski[4] has made experiments on the emission of light when sodium chloride is precipitated from aqueous solution by alcohol or by hydrochloric acid. When the precipitation takes place under suitable conditions of concentration and temperature, a bluish white light is emitted. This is so like the bluish luminescence of sodium chloride that one is tempted to look upon the two lights as the same. Owing to the faintness of the light it is very

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[1] Jour. phys. Chem. *13*, 703 (1909).
[2] Arnold: Wied. Ann. *61*, 326 (1897).
[3] Drude's Ann. *17*, 199 (1905).
[4] Zeit. phys. Chem. *15*, 325 (1894).

difficult to be sure of this fact; but a confirmation, such as it is, may be found in the fact that Bandrowski obtained a greener light when potassium chloride was substituted for sodium chloride. This change is in the right direction because Lenard found that fused potassium salts emit a green light and that a green light can be obtained with potassium salts in the Bunsen flame. Wiedemann and Schmidt[1] obtained a green light when potassium bromide was exposed to cathode rays. Beilby[2] reports that potassium bromide gives a green light when exposed to the action of beta and gamma rays. Experiments made in my laboratory have led to somewhat different results. We find that cathode rays produce a whitish light with potassium chloride[3], a blue light with potassium bromide, and a green light with potassium iodide. Since our results agree with those of Wiedemann and Schmidt for potassium chloride and potassium iodide, and since a trace of potassium iodide in potassium bromide would cause the green color, it seems to me quite probable that the alleged green light for potassium bromide was due to an impurity of iodide in the experiment of Lenard, Beilby, and Wiedemann and Schmidt. The salts used by Beilby were undoubtedly impure because he obtained a pink luminescence with potassium chloride, a result which nobody has confirmed.

The question of impurities is of relatively little importance in comparison with the fact that any given sample emits substantially the same light when exposed to cathode rays, when fused, when precipitated from aqueous solution, when placed in the proper part of the Bunsen flame, and when formed by direct combustion under suitable conditions.

In the case of the fused salt and in the case of the precipitation of the dissolved salt, only one reaction seems possible. We are dealing with the change from the ion to the undissociated substance. There is of course no reason why the cathode rays should not disintegrate sodium chloride into sodium as ion and chlorine as ion. It has been proved that lead sulphate is decomposed into lead and the acid radical and it is more in line with our usual way

[1] Wied. Ann. *56*, 205 (1895).
[2] Proc. Roy. Soc. *74*, 511 (1905).
[3] This was also noticed by Wiedemann and Schmidt.

of looking at things to postulate SO_4'' as ion. The more serious difficulty comes when we consider the slow combustion of sodium in chlorine or oxygen. In order to bring these results in line with the others, we must assume that the reaction between sodium and chlorine or oxygen takes place in at least two stages, sodium as ion being one intermediate product. This is not really a far-fetched assumption. We make a similar one in regard to reactions of metals or gases in aqueous solution. It is a necessary assumption if we are going to consider the formation and decomposition of sodium chloride as a reversible process.

If the change from sodium as ion to the undissociated compound is the reaction which emits the bluish luminescence, we apparently have the change from electrically neutral sodium vapor to sodium as ion as the reaction causing the yellow light which we ordinarily associate with sodium. This would be a legitimate conclusion if we could be certain that there was only one reaction to be considered. This is not the case. Lenard[1] has shown that there are several sodium spectra and the experiments of Wood and Galt[2] on the fluorescence of sodium vapor lead to the same conclusions. A good deal of work must be done before we can state specifically the reaction corresponding to each spectrum or spectrum series. On the other hand there seems to be no danger of there not being enough possible reactions. J. J. Thomson[3] has recently shown that we have at least nine different substances when a current passes through oxygen gas: neutral molecular oxygen, O_2; neutral atomic oxygen, O; atomic oxygen with one positive charge, $O^{\cdot}$; atomic oxygen with two positive charges, $O^{\cdot\cdot}$; atomic oxygen with one negative charge, O'; molecular oxygen with one positive charge $O^{\cdot}_2$; ozone with one positive charge $O^{\cdot}_3$; polymerized oxygen with one positive charge, $O^{\cdot}_6$; free negative corpuscles.

When sodium burns slowly in chlorine or oxygen, the change from sodium as ion to the undissociated compound is the only reaction taking place with sufficient rapidity to cause the emission of light. When the combustion is more rapid, we get the emission

[1] Drude's Ann. *11*, 636 (1903).
[2] Astrophys. Jour. *33*, 72 (1911).
[3] Chem. News, *103*, 265 (1911).

of yellow light which corresponds to the second, as yet unformulated, reaction. The intensity of this light is relatively so high that it ordinarily masks the continuous spectrum[1] having a maximum in the blue.

The work of Pringsheim[2] brings out clearly the relation between the flame spectra of sodium salts and the combustion spectra. Pringsheim showed that the illuminating gas in the Bunsen flame reduced the sodium salts and that the yellow light was due to the oxidation. Out in the oxidizing zone of the Bunsen flame we have rapid combustion and consequently we get the yellow light just as we do when sodium burns rapidly in chlorine or oxygen. At the surface separating the reducing zone and the oxidizing zone, we have the lowest rate of oxidation and consequently we should expect to find, what Lenard actually found, the same luminescence which is obtained when sodium burns slowly in chlorine or oxygen. We are not limited now to the chemical reactions which were known twenty years ago and we do not have to postulate a reaction between sodium and another chemical element in order to account for the yellow light. The value of Pringsheim's work consists in his conception that the reaction causes the light.

In the beginning of this paper I stated that the bluish luminescence is modified but slightly by the nature of the acid radical. This is purely an empirical statement; but it is one which is made as a first approximation by all workers in this field. Thus Wiedemann and Schmidt[3] conclude from their work with cathode rays that "in general the color of the luminescence of salts of the same metal is the same. The acid radical has an effect only on the intensity of the light. That some salts of a given metal luminesce while others do not is probably an effect of the acid radical." Lenard[4] found that the light was usually dependent only on the metal and not on the acid.

Of course, the generalization that the luminescence of a salt under various conditions depends only on the nature of the metal can only be true when the light emitted by chlorine, oxygen,

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[1] Lenard: Drude's Ann. *17*, 208 (1905).
[2] Wied. Ann. *45*, 428 (1892).
[3] Wied. Ann. *56*, 205 (1895).
[4] Drude's Ann. *17*, 203 (1905).

etc., is negligible. While this is ordinarily the case, Lenard found specific effects due to the acid in the case of phosphates and borates. "The phosphates and borates belong in a special class. In the case of the salts previously mentioned, the color emitted by the fused salt was determined by the metal alone. With the phosphates and the borates, the acid is not only a factor in determining the color of the emitted light; but is the predominant factor. Potassium phosphate emits blue light in the reduction zone and green light in the oxidation zone; while white light is obtained in the fusion zone, presumably owing to the clouding. Precisely the same effects are obtained with phosphoric acid alone (I used metaphosphoric acid containing a little sodium). Potassium borate remained transparent and dark for a long while in the flame but finally began to emit blue light. It was found however that by that time practically all the potassium had vaporized from the bead and that both the blue light and the green light could be obtained equally well with pure boric acid. Lithium borate and sodium borate also emitted blue light."

Wiedemann and Schmidt's own experiments with cathode rays show that their generalization is only a first approximation. Thus they obtained a white luminescence with potassium chloride and a bright green one with potassium iodide; a yellow one with lead bromide and a beautiful green one with lead iodide. As has already been stated, we find that cathode rays cause potassium chloride to fluoresce bluish-white, potassium bromide bright blue, and potassium iodide bright green. We have not had time to go into this matter carefully, as yet; but it seems probable that the green color observed with some iodides may be connected with the fact observed by Salet[1] that there is a green color in the oxidizing zone when a mixture of hydriodic acid and hydrogen burns in the air. Salet showed the formation of iodic acid under these circumstances; but if the color is due to a reaction of the iodine, it might be obtained under other conditions. A careful quantitative study of luminescence will doubtless show slight differences due to each acid radical. It is quite possible that the specific effect due to chlorine has been overlooked, because it produces whitish light.

[1] Comptes rendus, *80*, 884 (1875).

Trautz[1] considers all cases of luminescence during crystallization (crystalloluminescence) as cases of triboluminescence or luminescence produced by crushing crystals. In view of what we have seen of the relation between crystalloluminescence, luminescence due to cathode rays, luminescence due to combustion, etc., it is clear that the hypothesis of Trautz cannot be maintained in its present form. I see no objection to wording the hypothesis in another way. I should prefer to say that, in some cases, triboluminescence is the same as crystalloluminescence. When two crystals are rubbed together, one will become electrified positively and the other negatively. One way for this electrification to take place would be by a dissociation, sodium as ion going to one crystal and chlorine as ion to the other. A recombination, or an oxidation of the sodium, would then cause an emission of light which should be the same in quality as the light emitted under some other conditions. There is no difficulty about confirming this if we stick to sodium salts, because most triboluminescence is apparently bluish-white. Owing to the relatively faint light emitted as triboluminescence, it is very difficult to decide whether potassium iodide, for instance, gives a green light or the mercury halides an orange light. We hope to get definite evidence on this before long; but, for the present, a definite statement is not possible. In the case of sugar and substances of that type, luminescence in the Bunsen flame could not be the same as triboluminescence; but I should expect the triboluminescence to coincide in quality with the luminescence produced either by cathode or by the canal rays as the case might be.

The general results of this paper are:

1. The same bluish light is emitted: when sodium burns slowly in chlorine; when sodium chloride is fused; when sodium chloride is placed in the surface separating the oxidizing and the reducing zones of the Bunsen flame; when sodium chloride is precipitated from aqueous solution by alcohol or by hydrochloric acid; when sodium chloride crystals are crushed.

2. The reaction producing the light in all these cases is the change from sodium as ion to undissociated sodium chloride.

3. The light effect due to the change from chlorine as ion to

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[1] Zeit. Elektrochemie, *11*, 307 (1905); Zeit. phys. Chem. *63*, 12 (1908).

undissociated sodium chloride seems to be negligible for the present. More accurate measurements will undoubtedly show the existence of such a light effect.

4. Cathode rays excite the bluish luminescence in sodium chloride and canal rays the yellow luminescence.

5. The bluish luminescence in the Bunsen flame is found where the rate of oxidation of reduced sodium salts is lowest, at the surface between the reducing zone and the oxidizing zone. The yellow luminescence is observed in the oxidizing zone, where the rate of oxidation is higher. This is in harmony with Pringsheim's experiments on the radiation of sodium.

6. The simplest assumption in regard to the reaction producing the yellow sodium flame is that it is due to the change from sodium to sodium as ion. This hypothesis is inadequate because it does not take into account the other spectra of sodium observed by Lenard and by Wood.

7. Under the influence of cathode rays potassium iodide emits green light. Part of this light is probably due to the iodine. It seems possible that the chlorine may be the cause of some of the white light observed with many chlorides.

8. While it is probable that the crystalloluminescence and the triboluminescence of potassium iodide are the same as the cathodoluminescence of this salt, the experimental evidence is as yet insufficient.

THE EFFECT OF BROMIDE

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When we consider the effect of potassium bromide on the silver bromide, it is easy to see that bromide should act as a restrainer. The difficulty comes in when we consider different developers. In general we can say that a given amount of bromide has less effect with a fast developer than with a slow one.[1] In more or less accordance with this is the fact that metol, pyrocatechol, amidol, rodinal, and adurol are said not to be affected much by bromide while bromide has a marked effect with ferrous oxalate, pyrogallol, hydroquinone, glycin, ortol, and eikonogen.[2] In fact, bromide has little effect on a hydroquinone developer which has been made to work faster[3] by the addition of caustic alkali.

When we come to the data of von Hübl,[4] we get into trouble. Plates were exposed under a plate tester having a paper scale and were developed until some selected field could be seen. The potash developers contained 5g. potassium carbonate per 100 cc solution in excess of what was necessary to saturate the organic reducing agent. The developers with caustic alkali contained the amount of sodium hydroxide theoretically necessary to convert the organic reducing agent into a phenolate. The amidol developer of course contained no alkali; the ferrous oxalate developer was made according to Eder's formula. The temperature of development was 20°. The data are given in Table I.

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[1] Cf. Reiss: Die Entwicklung der photographischen Bromisilber-trockenplatte und die Entwickler, 105 (1902).

[2] Reiss: Ibid., 91, 96, 100, 105, 108, 68, 72, 85, 110, 94, 87 (1902).

[3] Reiss: Ibid., 83 (1902).

[4] Die Entwicklung der photographischen Bromsilber-Gelatine-platte, 3rd. Ed. 45 (1907).

TABLE I

Developer	Time of Development	Retardation by 0.2% KBr. Absolute	Percentage
Catechol, Na	15 sec.	5 sec.	33%
Metol, P	20 sec.	5 sec.	25%
Edinol, P	20 sec.	20 sec.	100%
Hydroquinone, Na	25 sec.	110 sec.	440%
Amidol	30 sec.	50 sec.	166%
Adurol, P	30 sec.	30 sec.	100%
Para-amidophenol, P	40 sec.	70 sec.	175%
Rodinal, *k*	40 sec.	45 sec.	112%
Pyrogallol, P	40 sec.	35 sec.	87%
Glycin, Na	45 sec.	90 sec.	200%
Eikonogen, P	50 sec.	85 sec.	170%
Pyrocatechol, P	60 sec.	140 sec.	233%
Hydroquinone, P	70 sec.	95 sec.	136%
Diphenal, *k*	75 sec.	30 sec.	40%
Glycin, P	75 sec.	210 sec.	280%
Ferrous oxalate	75 sec.	280 sec.	373%
Diogen, P	95 sec.	115 sec.	121%

P=potash; Na=caustic soda; *k*=solution as purchased.

Since it did not seem to be rational to compare absolute retardations, I have added a column of percentage retardations, obtained by dividing the time of development without bromide into the increase of time when bromide is present. A glance at Table I will show that there is no relation between time of development and either absolute or percentage retardation. On the other hand there is good reason for doubting the accuracy of these figures. Both the absolute and the percentage retardations are very high for the hydroquinone developer containing caustic soda and yet this is the one that Reiss says is not particularly sensitive to bromide. According to von Hübl the effect of bromide is greater when the hydroquinone developer is made up with caustic soda than when it is made up with potash. According to von Hübl, pyrogallol is not very sensitive to bromide whereas the contrary is known to be the case. Pyrocatechol with potash is apparently very much affected by bromide whereas Reiss says that it is not. It seems curious that the commercial rodinal solution should give the same time of development as the pure substance, *p*-amidophenol, and yet should behave so differently in presence of bromide. Though the absolute retardation is low with amidol, the percentage retardation is high. One cannot help feeling that this table does not represent the facts and that it is our ignorance of the facts that makes it difficult to account for the behavior of bromide.

One reason for the probable errors in von Hübl's table is the unfortunate selection of an endpoint. It would have been better to develop to a given, moderately high, density instead of to the point of visibility, because all our formulas for the relation between exposure, time of development, and density go to pieces for low densities. A more scientific line of attack was that adopted by Sheppard and Mees[1]. They showed that the presence of bromide shifted the whole of the density-exposure cure and they determined the amount of the shift. "It was shown that, over a certain range of exposure, bromide produces for the same time of development an equal or constant depression of density, or generally the exposure curve is referred to as a new origin. The shift was found to be, with ferrous oxalate, directly proportional to the concentration of bromide, and inversely proportional to the time of development. Hence, knowing the development constants K and $\gamma\ \alpha$ for a given plate, and also knowing the depression produced by bromide at a given degree of development γ for a given concentration, then the depression or any other degree or concentration, within limits may be calculated. By this means, if the depression with other developers be measured, then the concentration of bromide necessary to produce with ferrous exalate the *same* depression at the *same* degree of development can be calculated, and hence a numerical measure of the reducing energy of the developer compared with that of ferrous oxalate."

The concentrations of bromide required to produce the same depression as 0.01 nKBr with ferrous oxalate are: ferrous oxalate 0.01n; hydroxylamine 0.0113n; hydroquinone 0.0052n at 34 per cent development and 0.0070n at 40 per cent development; rodinal 0.034n. From these data Sheppard and Mees conclude that

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[1] Investigations on the Theory of the Photographic Process, 190 (1907).

rodinal is much the most energetic of the developers tried, while hydroxylamine comes next and hydroquinone has only one-half to two-thirds the energy of ferrous oxalate. It is not clear why Sheppard and Mees should consider the retardation by bromide as a measure of the energy of the developer; but fortunately that is not our problem.

In the experiments referred to, Sheppard and Mees arranged the relative concentrations of ferrous oxalate and of rodinal so that the speeds of the two developers were about equal. Since the effect of bromide was much less marked with rodinal than with ferrous oxalate, it seems to follow that part of the effect of bromide is specific to the developer. This is confirmed by the fact that Sheppard and Mees found that bromide has a very marked effect on a developer containing hydroquinone and caustic soda, though this is contrary to the previously quoted statement of Reiss. Unfortunately, Sheppard and Mees make no reference to Reiss's book and the two cases are not quite parallel because the rapid hydroquinone developers, to which Reiss refers, contain relatively more caustic alkali than does the solution of Sheppard and Mees; they also contain sulphite and ferrocyanide, either of which may have an effect. In the case of diamidophenol Balagny[1] states that bromide has a marked effect when the concentration of sulphite is low and has relatively little effect when the concentration of sulphite is high.

The general results of this paper are:

1. The effect of potassium bromide on the solubility of silver bromide may account qualitatively for the retarding effect of bromide with any given developer; but it is not sufficient to account for the relative behavior with different developers.

2. The general belief is that bromide has less effect with fast developers than with slow developers; but the general belief does not distinguish between absolute and percentage retardation.

3. The experiments of von Hübl do not show any relation between time of development without bromide, and either absolute or percentage retardation with bromide. The experiments are not in accord with general experience and there is good reason to suppose that they may be inaccurate.

[1] Monographie du diamidophenol en liqueur acide, 14 (1907).

4. The inaccuracy of von Hübl's experiments is probably due to the selection of a bad endpoint. It is difficult to make an accurate qualtitative determination of the time at which a given field in a sensitometer first becomes visible.

5. The experiments of Sheppard and Mees show a different action of bromide with ferrous oxalate and rodinal even when the relative concentrations of the developers have been adjusted so that the speeds are practically identical without bromide. This indicates a specific effect of the bromide upon the developers.

6. With diamidophenol as developer the effect of bromide varies inversely as the concentration of sodium sulphite.

7. There is no theory at present to account for a specific action of bromide on a developer. Before one can be put forward, we need accurate data to show whether such a specific action exists and, if so, how it varies with the nature and concentration of the developer and of the other substances in the solution.

THE LATENT IMAGE

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With a short exposure to light we get a latent image which develops to a negative; with a longer exposure we get a latent image which develops to a positive. Since the action of light can be duplicated by the action of any suitable reducing agent[1], the latent image cannot be another modification of silver bromide; but must be a reduction product. The latent image cannot consist of metallic silver as a second phase, because the latent image does not show the chemical reactions of metallic silver, because it does not show the electrical potential of metallic silver, and because this hypothesis cannot be reconciled with the facts of solarization.

While Luther's earlier experiments pointed to the existence of the definite compounds Ag_2Cl and Ag_2Br, the more recent work from the same laboratory[2] has shown their non-existence. Reinders[3] found no evidence of the existence of any stable compound of silver and silver chloride either at high or at low temperatures. The reactions of the latent image[4] are not consistent with the existence of a compound having the formula Ag_2Br. It is also impossible to account for the phenomena of solarization on the assumption of only one compound, no matter what composition may be assigned to it. This has been admitted by Trivelli[5] who gets around this difficulty by postulating the existence of four compounds, Ag_8Br_7, Ag_8Br_6, Ag_8Br_5 and Ag_8Br_4. As these alleged compounds have never been prepared in a state of purity and as there is no satisfactory evidence as to their existence, we are justified in ignoring them and we therefore conclude that the latent image is a phase of variable composition

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[1] Perley: Jour. Phys. Chem. *14*, 689 (1910).
[2] Heyer: Jour. phys. Chem. *15*, 557, 560 (1911).
[3] Zeit. phys. Chem. 77, 213 (1911).
[4] Cf. Jour. Phys. Chem. *15*, 560 (1911).
[5] Cf. Lüppo-Cramer: Das latente Bild, 23 (1911).

with silver bromide as the end term. This view was first suggested by Carey Lea[1] and has been brought into prominence by Lüppo-Cramer. It is the view adopted by Reinders[2] as a result of his recent experiments.

There has been a good deal of discussion whether the constituents of the new phase are silver bromide and silver or silver bromide and some unspecified sub-bromide. This is rather a waste of time as we have no way of distinguishing between these two hypotheses. If one insists on specifying the constituents, it is at least simpler not to assume a hypothetical sub-bromide. There is also the further advantage that one can connect the colors of the photohalides with the colors of colloidal silver[3].

The photohalides have been made synthetically and it has been shown that their reactions are the same as those of the latent image. Since the latent image is neither pure silver bromide nor pure silver, it is not surprising that its reactions should differ somewhat from those of the constituents. Most of the arguments against the latent image being a reduction product are arguments against the existence of silver or of a definite subhalide and they lose their force in the case of a phase of variable composition. People have claimed that the exceedingly minute amount of sub-bromide produced by ordinary exposure is a weak point in the decomposition theory and that it is very far from sufficient to furnish by itself an image that can be seen or discovered in any way, except by allowing it to grow.[4] Since the whole grain is affected, this difficulty disappears as does the point raised by Namias[5] that stannous chloride converts a plate into a developable condition even when only one one-thousandth of the total amount of silver bromide can have been converted into sub-bromide. The energy calculations of Messrs. Hurter and Driffield[6] lose their force now that we assume that an almost infinitesimal change in the composition of the silver bromide grain is sufficient to make development possible. Since we can develop

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[1] Am. Jour. Sci. (3) *33*, 349 (1887).

[2] Zeit. phys. Chem. *77*, 213, 256, 677 (1911).

[3] Reinders: Zeit. Phys. Chem. *77*, 363 (1911).

[4] Cf. Chapman Jones: Science and Practice of Photography, 374, 387 (1902).

[5] Phot. Correspondenz, *43*, 155 (1905).

[6] Cf. Jour. Phys. Chem. *15*, 355 (1911).

the whole of the grains which have received a sufficient exposure and since we cannot develop the unexposed grain there is nothing surprising in the fact that it is common experience in the development of a gelatine plate that a time comes when the development is complete. There is also no reason why the growth of the image should go on until the reduction of the silver salt is complete, and the plate is evenly black all over. Yet this objection has been raised by Chapman Jones and by Namias[1], to mention no others.

I have already shown that all the phenomena of solarization can be accounted for on the assumption that certain compositions are less rapidly reduced than others which contain more or less silver. This is a perfectly familiar phenomenon where we have a series of compounds as in the reduction of nitrobenzene. Nitrosobenzene is more rapidly reduced to aniline than is nitrobenzene though the latter contains more oxygen, while hydrazobenzene is less readily reduced than phenylhydroxylamine though this latter contains more oxygen. There is one point however, which requires a correction. For the sake of simplicity and because I knew no better, I followed Eder and assumed[2] that the second negative was metallic silver before development. I am satisfied now that that was an error and that the visible image on a bromide plate is merely a blackened grain which is capable of development. The only difference that this introduces is that it now becomes theoretically possible to have any number of reversals, while a second positive was theoretically impossible under the original assumption.

In all discussions on solarization up to now, people have made qualitative statements. Now that we know what the latent image is, it ought to be possible to determine approximately at what composition we get a positive with any given developer. I had thought of getting at this by melting an emulsion, exposing it to light, and afterwards analyzing for bromide. This would have presented experimental difficulties and I was fortunate enough to find that Lüppo-Cramer[3] had obtained the data for me in a

[1] Cf. Jour. Phys. Chem. *15*, 341, 350 (1911).
[2] Jour. Phys. Chem. *13*, 461 (1909).
[3] Phot. Correspondenz, *46*, 526 (1909).

more satisfactory way. Lüppo-Cramer made up silver bromide emulsions containing known amounts of colloidal silver taken up by the silver bromide. When the silver bromide contained 0.002 per cent silver synthetically, there was a distinct fogging on development. With increasing amounts of silver the rate of blackening in the developer increased and the sensitiveness to light increased until a maximum was reached at about 0.1 per cent silver. An emulsion containing 0.1 per cent silver is about twenty-five times as sensitive as one containing 0.4 per cent silver. This gives the necessary figures for this type of emulsion and for the developer used. From 0.002-01 per cent silver we are dealing with the first negative. Somewhere just beyond 0.1 per cent silver we pass to the first positive. It is interesting to note that this is about the value usually given for the maximum decomposition when one is to develop a negative.

We also have a developable latent image produced by the action of acids, of heat, of pressure, etc; but I doubt this image being the same as the ordinary latent image. We know that precipitated silver bromide, containing no gelatine, is reduced almost as rapidly before exposure to light as after exposure. We know that in an emulsion the silver bromide grain contains gelatine and water. Anything that will remove the gelatine will cause the silver bromide thus treated to develop more rapidly than the remaining silver bromide. I think that this is what happens in the cases just cited and that we do not have a true latent image in the sense of a partially reduced silver bromide. This view is confirmed by some results obtained by Lüppo-Cramer.[1]

"An exposed silver bromide gelatine plate, on which I had as usual left a broad unexposed strip, was placed for half a minute in a dilute nitric acid (8.3 per cent). The gelatine was attacked but remained on the plate. The plate was washed thoroughly and was developed along with another from the same emulsion, which had received the same exposure but which had not been dipped in nitric acid. I obtained the entirely unexpected result that the plate, which had been dipped in acid, blackened even on the portions which had not been exposed, while the unexposed strip

[1] Cf. Jour. Phys. Chem. *15*, 574 (1911).

of the check plate remained quite clear. The same result was obtained even when the solution contained only one half to one fourth per cent nitric acid and though no change in the gelatine was then visible. The effect disappeared when an extremely dilute nitric acid (0.05 per cent) was used. A fogging of the unexposed silver bromide was also obtained by means of sulphuric acid but the sulphuric acid does not produce as marked changes in the gelatine as the nitric acid nor does it fog the plate so much. A 10 per cent sulphuric acid is approximately equivalent to an 0.5 per cent nitric acid. A 5 per cent ammonium persulphate solution is about equivalent to these acids."

Lüppo-Cramer[1] agrees with me in believing that a true latent image is not formed by pressure. He says that the pressure phenomena can be distinguished from real reduction phenomena because the latter occur throughout the whole film and are not changed in the slightest by any rubbing of the surface.

Lüppo-Cramer[2] has found that the latent image can be developed by light provided a solution of a bromine absorber, such as sodium nitrite, be added. He thinks that this is a puzzling thing. It does not seem so to me. The action of a uniform light on a previously exposed plate merely shoves the whole thing along. The picture which he obtained was undoubtedly flatter than the one he would have got by straight development, because the percentage differences in the exposures decreased with the increasing time that the uniform light was allowed to act. It is also a question whether he really developed to a silver image or not; but there is nothing difficult about the theory of the process.

One objection to identifying the latent image with the photohalides is that the latter are often brilliantly colored, while the former never is under ordinary conditions. The answer to this seems to be that the color of the photohalides depends on the color of the adsorbed colloidal silver and that we are interested especially in preparing brilliant photohalides while the conditions in the photographic plate are ordinarily such that we get a dull colored photohalide. This is confirmed to a certain extent by the fact that Lüppo-Cramer[3] has obtained a pink color by the

[1] Phot. Correspondenz, *40*, 180 (1903).
[2] Das latente Bild, 10 (1911).
[3] Phot. Correspondenz, *48*, 353 (1911).

action of Röntgen rays or of ultra-violet light on certain plates.

Photoretrogression is due to the latent image reacting with the halogen. The real problem is where the halogen comes from. It does not seem to me probable that any very appreciable portion comes from the decomposition of a bromo-gelatine compound. It seems probable to me that a certain amount of the bromine set free by light remains temporarily adsorbed in or on the silver bromide grain or on the silver bromide which was not exposed to light. Ordinarily it passes off into the air or reacts with gelatine; but it may react again with the latent image if conditions are favorable. At first sight it seems improbable that the bromine could be adsorbed by the decomposed silver bromide without reacting with it; but this may be the case. We know, for instance, that free chloral and free water coexist dissolved in chloral hydrate. We know that acetic anhydride and water take hours to react completely when dissolved in acetic acid. The data are not sufficient for me to give a final answer to this question. I can point out that, since the amount of bromine adsorbed will be small, photoretrogression will be more marked with under-exposed pictures than with others. Since iodine is adsorbed strongly by silver iodide,[1] this may be the reason why photoretrogression is especially marked with emulsions containing some iodide.[2]

Bredig[3] once suggested that the developability of the latent image may be the result of a physical disintegration of silver bromide by light. This idea has recently been taken up by Lüppo-Cramer[4] who now lays great stress upon it, as a result of experiments with Röntgen rays. There is no doubt that light or other radiations may disintegrate silver salts and thus produce a developable image. It is possible that this may be an important factor in the case of the Röntgen rays, but I see no reason to suppose that it is of any importance under ordinary photographic conditions.

The general results of this paper are:

1. The latent image is not metallic silver, a sub-bromide, or another modification of silver bromide.

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[1] Cf. Goldstein: Jour. Phys. Chem. *13*, 54 (1909).
[2] Cf. Barker: Jour. Phys. Chem. *15*, 323 (1911).
[3] Eder's Jahrbuch der Photographie, *13*, 365 (1899).
[4] Das latente Bild, 2 (1911).

2. The latent image is a phase of variable composition, presumably due to absorption of silver by silver bromide.

3. The latent image is identical with the photohalides except as to color.

4. The latent image which gives rise to a negative under normal development consists of silver bromide with an excess of about 0.002-0.1 per cent silver.

5. The latent images produced by heat, acids, pressure, etc. are not true latent images because they do not involve a change in the ratio of silver to bromine. They are due to the removal of gelatine, etc, from the silver bromide grain.

6. Development by means of light and sodium nitrite presents no theoretical difficulties.

7. There are not sufficient facts available to permit a really satisfactory discussion of photoretrogression.

8. Under ordinary conditions the mechanical disintegration of silver salts by light is not an important factor in the production of a latent image.

THE PERMANENCY OF PAINTINGS

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When light is absorbed by a substance, the substance tends to change and consequently there is a tendency for light to affect all pigments. Since the light produces but a relatively small change in the chemical energy, it depends on the special conditions whether any given pigment is affected or not. There is no particular type of reaction produced by light of any given wavelength. It is not true, for instance, that the blue rays have a reducing action and the red rays an oxidizing action. Light may cause or accelerate an oxidation, a reduction, an allotropic change, a dissociation, a condensation, or a metathetical reaction. The change that takes place depends entirely on the chemical conditions prevailing while the pigment is exposed to light. Methylene blue, for instance, may fade as a result of reduction[1] or of oxidation. The bleaching of methylene blue is usually an oxidation because of the oxygen in the air. In presence of gelatine[2] or of stronger reducing agents the bleaching of methylene blue by light is due to a reduction. On standing in the dark the leuco base is oxidized and the color comes back.

In the case of water colors, the change due to light is usually an oxidation. It seems possible that the rapid fading of water colors may be due in part to the gum[3] acting as an oxygen carrier. This should be looked into, because it might be possible to use some substitute for gum which would not produce such harmful results.

With oil paints we may get a reduction in case the oil contains a drier. The drier acts as an oxygen carrier to oxidize the oil. In addition to taking oxygen from the air, it may reduce the pigment especially if the supply of oxygen be limited. We get an admirable instance of this with Prussian blue.[4] "When Prussian

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[1] Cf. Wender: Jour. Chem. Soc. *66*, II, 122 (1894).
[2] Gebhard: Zeit. phys. Chem. *79*, 649 (1912).
[3] Cf. Struve. Liebig's Ann. *163*, 160 (1872).
[4] Toch: Materials for Permanent Painting, 152 (1911).

blue or any of its analogues are mixed with white lead or flake white, the rich sky blue or greenish tint which will result bleaches over night into a sickly green; but, on exposure to the light for an hour, it comes back to its original color."

Here the white lead acts to a certain extent as a drier. Under some conditions a slight reduction of ferric oxide takes place[1]. "Upon long and extreme exposure the bright Indian red loses its brilliancy and turns darker, which is due to the chemical change or decomposition from the ferric to the ferrous state. The ferrous [ferro-ferric] oxide of iron is a black oxide with which the artistic painter is not acquainted. The ferric oxide of iron is the bright red oxide. The darkening effect of Indian red is due to the slight change from the ferric to the ferrous [ferro-ferric] oxide. The same is true when Indian red is mixed with zinc oxide to produce a flesh tint. The author exposed a sample so made for three years to the bright daylight, and at the end of three years a very slight darkening had taken place; but, inasmuch as artistic paintings are rarely, if ever, exposed to the bright sunshine throughout the entire year, Indian red must be regarded as one of the permanent and reliable pigments." Toch[2] also states that "driers decompose many pigments. In fact, nearly every one of the lake colors is rapidly affected by the action of driers. Madder Lake, when mixed with a lead or manganese drier, soon loses its pristine brilliancy." In presence of oxygen the drier oxidizes the pigment. In presence of oil and only a slight amount of oxygen, the drier reduces the pigment and oxidizes the oil.

With vermilion we have an allotropic change from the red form to the black. It appears to take place more readily in water colors[3] than in oils. "In water-color painting most vermilions are found to be changed on exposure, the solar rays gradually converting the red into the black modification of mercuric sulphide, without, of course, producing any chemical alteration. This change occurs even in the absence of air and of moisture. Impure air, *per se*, even if sulphuretted hydrogen be present, does not discolor vermilion. Any one who has examined old illuminated

[1] Toch: Materials for Permanent Painting, 132 (1911).
[2] Materials for Permanent Painting, 75 (1911).
[3] Church: The Chemistry of Paints and Painting, 3rd Ed. 169 (1901).

manuscripts must have noticed the apparent capriciousness with which the ornaments, and especially the initial letters, painted with vermilion, have been affected. I have more than once observed that, while all the vermilion used in one part of a missal or choral-book has remained red, a leaden hue has spread irregularly over the rest of the work in places where this pigment has been used. This may be due to the use by the illuminator of a sample of vermilion adulterated with minium or red lead, but sometimes to a change in the technique, as a change in the style or handiwork is often associated with the difference above described. In oil painting there are no permanent pigments, save the copper-greens, with which vermilion may not be safely mixed. Only when it contains impurities, such as free sulphur, does it darken flake white.

"Vermilion prepared from native cinnabar is found perfectly preserved in the flesh tints of Italian tempera-paintings of the thirteenth and fourteenth and fifteenth centuries. It has stood in the wall-paintings of Pompeii, where it often seems to have been waxed. A comparatively recent but instructive instance of the permanence of vermilion in oil is furnished by a portrait dated 1758, in the National Museum Gallery. It represents the painter, Hogarth, with his palette set before him. The second of the dabs of color thereon is vermilion, perfectly intact. In the small collection there is a portrait by Marc Gheeraedts of Mary Sidney, Countess of Pembroke, in which the vermilion has stood. This work was painted in 1614. Scores of earlier and later examples might be cited."

Since the discoloring of vermilion is an allotropic change and is therefore independent of other reagents, it might seem as though vermilion ought always to be stable or always to be instable. I shall take up this point later when considering methods of preventing the light from changing pigments.

The case of carmine presents certain difficulties. There is no question but that carmine is instable in light. Church[1] says that "beautiful and rich as are the colors prepared from cochineal, not one of them should ever find a place upon the palette of the artist. They all become brownish, and ultimately almost dis-

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[1] The Chemistry of Paints and Painting. 3rd Ed. 186 (1901).

appear after a short exposure to sunlight or the more prolonged attack of strong diffused daylight. In six hours of sunshine a strong wash of fine crimson lake on Whatman paper lost 8 per cent of its original intensity; this was on April 12th. The loss during a second period of six hours' exposure was much less, but after the lapse of four months less than 5 per cent of the original color remained. In the case of carmine, from one to two years was required for the complete obliteration of every trace of the original crimson from a deep wash of this pigment. All the cochineal pigments become somewhat brownish during the course of fading, but ultimately, when all the red has disappeared, either a greenish grey or a faint sepia-like brown is the sole residue."

Notwithstanding this evidence as to the instability of carmine, there exists a tradition that a first-class grade of carmine can only be made in sunlight.[1] Never having seen carmine made, I do not know whether this belief is erroneous or what the explanation is in case the belief is true. The only guess which occurs to me is that the raw carmine contains some impurity which is more readily destroyed by sunlight than the carmine itself.

The permanency of pigments in light is complicated by the presence of gases in the atmosphere.[2] "In all large communities there exists sulphuric acid in the air, and many colors which we have regarded as permanent to light, are not permanent to the effect of acid gases. In a general way this rule applies also to the colors affected by sulphuretted hydrogen. If we take, for instance, red lead, which is the red oxide of lead, and expose it to the air of a city, it apparently bleaches white. The same red lead when varnished and covered with glass may be exposed for ages and will not be affected. We note the former change particularly on steel structures like bridges, which have been painted with red lead and on which the color sometimes bleaches from a pure scarlet to a pale pink. On rubbing such a surface with linseed oil and turpentine the original color comes back in all its brilliancy. Upon investigation, we find that the sulphuric acid formed a minute crystalline surface of sulphate of lead, which is white. Chrome yellow will be affected in the same way.

[1] Bersch: Manufacture of Mineral and Lake Pigments, 358 (1901).

[2] Toch: Materials of Permanent Painting, 181 (1911).

Improperly washed Prussian blue will likewise bleach, and flake white is affected in identically the same manner, with the exception, that the change cannot be noted by the eye, but if a flake white surface, which has been exposed to the elements, is rubbed with a black cloth, a white chalky deposit will stain the cloth. This is known as chalking and mural decorations which cannot very well be varnished and protected should therefore be executed with pigments that are not affected by the acid gases of sulphur. Nearly all the pigments are affected, with the exception of the blacks. The ochres, siennas and the earth colors, which are exceedingly permanent, show this defect although to a less degree, as compared with the chemical colors like Prussian blue, the lakes, cadmium yellow and the lead colors; but paintings which are kept in a pure atmosphere under glass are necessarily preserved, and water colors are more susceptible than any other form of painting."

The blackening of white lead by hydrogen sulphide can be counteracted to some extent by exposing the lead sulphide to light and air, in which case it is oxidized to lead sulphate.[1]

"My attention was directed to the action of light upon the sulphide of lead from observing that in the glass cases in the Technological Museum under my charge at the Crystal Palace, which are painted white with white lead, substances which emitted sulphurous vapors did not cause a darkening of the surface of the case, except where it was protected from the direct influence of light.

"In the case devoted to sulphur, for instance, the spaces obscured by the descriptive cards alone were blackened, the white color of the rest of the case being unimpaired. In the cases containing vulcanized rubber, wools, woolen fabrics, hair, and other animal products containing sulphur, the same appearances were presented.

"In the first-named of these cases I had placed the dried leaves of the gutta-percha plant, attached to a piece of cartridge paper—a translucent substance. Upon removing the paper I found a tolerably faithful photograph of the leaves upon the surface of the case.

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[1] Price: Jour. Chem. Soc. *18*, 345 (1865).

"In order to verify these observations, and to gain a knowledge of the cause and rapidity of the action, and at the same time to ascertain the effect of the colored rays upon sulphide of lead, the following experiments were made:

"A board painted white with white lead and oil was exposed in a chamber for several hours to the action of sulphide of hydrogen gas until the painted surface had acquired a nearly uniform chocolate or deep-brown hue. Plates of glass of different colors were then placed upon the painted surface, one portion being at the same time covered by an opaque medium, and another left open and unveiled to the light. The board was then placed in a situation facing the east.

"The glasses which I employed were of the following colors and properties: 1, red; 2, blue; 3, yellow; 4, violet; 5, a glass that diminishes the intensity of all the rays; and 6, a glass which slightly reduces the yellow ray. My friend, Mr. Robert Hunt, F. R. S., was kind enough to lend me the series of colored glasses which he employed in his investigations for the British Association, and the optical properties of which he had determined; but, with the above exceptions, I have not thought it requisite to record the results obtained, desiring rather to view the subject from a practical point. The results shown are from an exposure of eight days, on one of which only was the atmosphere clouded. It will be observed that the surface exposed to the action of light is now perfectly white, whilst that under the influence of the red ray remained as dark as where the sulphide had been protected from light. The blue ray has effected an almost complete conversion of the sulphide; the yellow ray a partial, and the violet considerably less action than the yellow. The light passing through glass 5 has produced somewhat less effect than has resulted from the blue rays, whilst with glass 6 the action has been nearly as rapid as where the surface has been left quite exposed to the light. The action of drying oils is very rapid upon sulphide of lead, an exposure to light for a few days only being sufficient to change a surface of it coated with a thin layer of linseed oil into a white one. When boiled linseed oil is used, still less time is required to effect the change. That the action is an oxidizing one there can, therefore, be little doubt, and I regret that I have not been able to get the further proofs on this point ready for this occasion, but knowing that there are many in Birmingham who might be interested in the subject, I have thought it better not to defer the communication of these results on that account. It is however, not only when mixed with oil that the conversion of the sulphide is accomplished, for where water color was used, the action was still marked, although slow, as will be seen by the illustration exhibited, in which the dark spaces were protected from the light by cards and other opaque substances.

"These observations serve to explain part of the evidence given before the 'Royal Commission appointed in 1857 to report upon the Site best adapted for the National Gallery,' in reference to the facts stated by directors of galleries, artists and picture-dealers, as to the injury which pictures suffer by being kept in ill-ventilated and badly lighted places, and of the beneficial effects resulting, in many instances, from the exposure to direct sunlight of injured pictures.

"From this report I quote the following: Mr. Knight, the Secretary of the Royal Academy, stated that he preferred pictures to be exposed to the light if he wanted to preserve the lights of a picture. Mr. Farrer mentioned a case where, by exposing a picture that had been kept in the dark, the blue became brighter. Sir Charles Eastlake, P. R. A., instanced the case of some of the pictures from the late Mr. Turner's gallery, those of 'The Deluge' and 'Queen Mab' in particular, where the whites were turned into blacks, and stated that white lead, if not tolerably well secured from the effects of the atmosphere, would undergo a rapid change in London, and that it was a very general opinion that pictures look better and last longer in the country than in London. Mr. Bentley, who restored these pictures by a secret and chemical process, said that the highest light was perfectly black and that, in fact 'high light' was 'high dark.'

"I have here an illustration to show that the changes effected by the secret and chemical process may be brought about by simple exposure of the picture to the light. The picture was placed in an atmosphere of sulphide of hydrogen gas until it had acquired a dark brown color, strips of paper were then fastened across parts of the surface, and it was placed in a window facing the light. Those portions not obscured, it will be observed, have resumed their original appearance, whilst those covered by the paper remain as black as when the paper was first placed over them.

"Mr. Cooke, P. A., stated that light is one of the greatest agents in the preservation of pictures; that it helps to develop them in every way, particularly with regard to the varnish, and he gave an instance of a picture of his own which he had lent for exhibition to a gallery where it had been exposed to a very strong light; that five months afterwards, when it was returned to him, he was surprised as its extremely bright appearance.

"In reference to the action of light on varnish mentioned by Mr. Cooke, I may observe that I have found that when light is excluded from a painted white surface, the surface assumes a dingy yellow color, but that the original color is restored by admitting the light to it. This fact is, I find from the report, acknowledged by many artists.

"I have said that the glass cases containing woolen fabrics were blackened, and it may be well to draw attention again to the fact, with a view of showing that no small source of sulphur vapor in the atmosphere of a gallery frequented as the galleries in London are, may arise from the clothes of the visitors."

"That the experiments which I have described, taken in conjunction with the testimony just read, have an important bearing upon the preservation of paintings, will, I think, be evident, as they demonstrate the protecting influence of light upon white lead and those colors with which it is mixed, where the atmosphere is or may become contaminated with sulphurous gases, and conversely the deterioration that paintings must suffer where under the same circumstances the light admitted is feeble — facts deserving of attention in the construction of galleries in the metropolis and large manufacturing towns, and by those who have the care of paintings in churches and public buildings, or who possess collections of their own, and adopt the practice of covering their pictures.

"It is curious to observe in many parts of London the discoloration of houses painted with white lead. I have frequently seen the lower portions completely coated with a metallic-like surface of the sulphide, and I have little doubt that the formation of this compound will be found to be more frequent in Winter than in Summer, and more prevalent on the shady than on the sunny side of a street."

The secret chemical process referred to by Price undoubtedly consisted in the use of an oxidizing agent. Hydrogen peroxide is the substance usually recommended for this purpose; but there is no reason why we should be limited to this oxidizing agent and, as a matter of fact, any oxidizing agent may do more harm than good[1] in certain cases.

"When sulphur fumes have decomposed the lead color and formed a brownish result, chemists have recommended the use of peroxide of hydrogen, and while this may be theoretically the proper method to pursue, it is not necessary, and sometimes dangerous, for the reason that even though peroxide of hydrogen will bring back flake white and chrome yellow to their original color, it may bleach an adjacent lake beyond redemption, and as these sulphur decompositions of color are usually on the surface, the wood alcohol and turpentine treatment with very slight abrasion, will produce all the results necessary. The cleaning and renovation of pictures in the hands of an intelligent person is not a very difficult problem, but it is very easy to spoil any good painting by the use of nostrums and recipes which are destructive in their effect."

A secret chemical process which works well in some cases is to take soap and water, and to wash off the extremely thin film of discolored pigment. The simplest way to prevent the formation of lead sulphide is not to use a color containing lead. On the painter's palette flake white has been practically superseded by Chinese white; but the less dangerous lemon yellow is still used.

The effects due to harmful gases in the air and to a varying dew point can be minimized by keeping paintings carefully varnished and by painting the back of the canvas.[2] If the pigments are not washed carefully when they are prepared, substances

[1] Toch: Materials for Permanent Painting, 61 (1911).
[2] Toch: Ibid. 182 (1911).

may be left in which will have a deleterious effect either on that pigment or on some other pigment with which it may later be mixed. This is responsible for some of the contradictory reports in regard to the permanency of certain colors. Aurelian and cadmium yellow are typical cases.[1]

"Aurelian is a pigment that has been introduced during the last generation, and is sometimes sold under the name of cobalt yellow. It is a double nitrite of cobalt and potassium. There is a variety of opinion as to its permanency. Some claim that it is absolutely permanent both in water and oil, and others claim that it decomposes with a white, but from the experiments made by the author its permanence depends entirely upon its purity. If the color is thoroughly washed by the manufacturer after it is precipitated in order to free it from soluble salts, it may be regarded as absolutely permanent, because it is not affected by sulphur gases nor by sunlight. If the color is impure, it is very likely to decompose any lake which may be added to it, and when mixed with raw linseed oil, it loses its brilliancy in a short time. There are several good manufacturers of this pigment, whose aurelian yellow may be used and regarded as absolutely permanent."

"Cadmium yellow may fail, and in some instances does fail, because it is improperly made and because it is ground in an emulsion of oil and water, or because the oil in which it is ground may be of a highly acid nature. Manufacturers of tube colors ought to learn the lesson that no tube color should be ground in a chemically bleached vegetable oil, for oils are principally bleached by means of a strong acid like sulphuric or chromic, and all traces of these acids are not entirely washed out, so that much trouble may arise from the ultimate effect of this trace of acid, and even a good color like cadmium may be decomposed if the oil be not entirely pure."

We can now consider some possible methods of cutting down the action of light on pigments. While all rays which are absorbed tend to decompose a pigment, the absorbed rays are not equally effective. In the bromination of organic compounds, the most effective rays are those corresponding to the weaker bromine absorption bands in the yellow-green and orange, instead of those corresponding to the stronger absorption bands in the greenish-

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[1] Toch: Materials for Permanent Painting, 90, 102 (1911).

blue and blue. If we should cover a pigment with some substance which would cut off the more effective rays, we should increase the permanency of that pigment to light very much. Though we have no quantitative spectroscopic study of this point, this case appears to occur with vermilion and madder.[1]

"Vermilion is a sulphide of mercury, and is artificially made by mixing sulphur and mercury in the presence of an alkaline solution under heat and pressure. It ranges in shade from a light orange to a deep scarlet, and while it is perfectly true that when used alone as an oil color and exposed to the brilliant sun rays, it will darken considerably, when glazed over with madder, as is frequently done after it is thoroughly dry, it is remarkably permanent, or when properly varnished it is very stable."

The varnish on a picture cuts off the ultra-violet light to a very great extent and protects the picture in this way, in addition to keeping out moisture and the gases in the air.

The yellowing of pictures is due to a change in the oil.[2] "That the cause is what may be termed the effect of light on a mixture of white lead, zinc oxide and linseed oil, or a linseed oil varnish, is evident because paint chemists have long known that white lead in any form, whether it be called flake white, cremnitz white, silver white or white lead, has a reducing action on the pigment present in linseed oil, or linseed oil varnish, and that this reducing action changes this pigment into another pigment which is yellow. It may fairly be asked whether such a reaction can take place if the linseed oil is bleached. To this question the reply must be given that the bleaching of linseed oil does not destroy the color which is present, but simply changes it from an olive yellow to an exceedingly pale yellow which can hardly be seen, so if we take refined or bleached linseed oil and mix it with white lead or zinc white we have a very brilliant white which remains white as long as it is exposed to bright light. If we take this mixture and place it for six weeks in an absolutely dark place, the white paint changes into the well-known yellow tint and it is this particular change which produces in all paintings the distinct yellowness of age."

[1] Toch: Materials for Permanent Paintings, 108 (1911).
[2] Toch: Materials for Permanent Painting, 33, 35, 38 (1911).

"Another line of experiments was carried out, in which bleached linseed oil was also used. This turned exceedingly yellow in three months, but when exposed for three months to the bright sunlight it became brilliant white again, and upon being placed in a dark closet for another three months no change took place. Those parts of the painted experiment which had been bleached by the sunlight remained white in the dark closet at the end of the experiment. This would therefore prove that when a picture has turned yellow it can safely be exposed to the sunlight in order to bring back its natural brilliancy, provided, of course, that no part of it has been painted with asphaltum or bitumen for the asphaltum and bitumen, instead of bleaching in the light, become black."

"If linseed oil is insisted upon by the painter the raw, unbleached, unrefined product should be used for it is reasonable to assume that it cannot grow any darker as long as the coloring matter is not visibly hidden, but may improve, for upon exposure the color will surely bleach, and upon replacing the painting in a poorly lighted room it will not grow any darker than it originally was when the painter used it."

These experiments raise the question whether a better way of bleaching might not be found which would destroy permanently the coloring matter in the oil.

Since the action of light on pigments is an oxidizing one in the majority of cases, the safest pigments to use are normally those which are made by oxidation and this is a point to be kept in mind when studying coal tar colors. While it is possible that the organic chemist may some day give us a series of colors which are absolutely permanent to light, it will perhaps also be well to consider whether we cannot increase the stability of all or some of the colors that we now have. The coal tar colors are used as pigments chiefly in the form of lakes. In spite of the importance of the matter we seem to have no definite, quantitative information as to the actual effect due to mordant or to base. In books on dyeing one finds isolated statements that such and such a dye is faster with one particular mordant than with another; but there are no general statements and no attempt at an explanation or theory.

We have found that some lake pigments are more fast to light than the corresponding dye is when dissolved in water; but there is no reason to suppose that this is generally true. Playfair[1] has shown that calcined alumina causes nitric acid to attack indigo. "A portion of alumina may be taken and placed at the bottom of a vessel containing warm NO_5 [HNO_3]; no action ensues, except partial solution; a strip of calico colored in indigo-blue may now be introduced into the mixture, and remains unaffected in the clear acid, but is immediately discharged when pressed with a glass rod into the alumina. Here the alumina acts by placing the oxygen of the nitric acid in a state of tension without, however, succeeding in decomposing it, but the moment an assistant affinity comes into play, that state is shown by the decomposition of the nitric acid and the oxidation of the indigo. The alumina in the presence of the acid could not oxidize (in fact we know of no higher oxide), and therefore the indigo appropriates the oxygen. I find that various other oxides, such as calcined Cr_2O_3 and SnO_2 have the same power, the latter showing this disposition more than any of the other oxides."

Of course, this experiment of Playfair's does not bear directly on the matter in which we are interested; but it is very suggestive and has an important indirect bearing. In a recent book[2] there is a statement that copper salts are known to increase the stability of all dyes to light. In view of the fact that copper salts act as oxygen carriers, I doubt the accuracy of this statement. It is important either way. If copper salts really do increase the stability of all dyes to light, we must get a theory to account for the fact. If they do not act in this way, the statement serves to illustrate our general ignorance in regard to the subject.

The whole question of double mordants, or of fixing agents, is also an important one. When we wish fastness to washing we know that we must add lime when we mordant alizarine with alumina. Methylene blue stands soaping if fixed by magnesium and aluminum acetates.[3] Orange No. 2 is fixed by chromium and magnesium acetates; chromium acetate *per se* gives a brown color; magnesium acetate *per se* does not fix the color. Grey

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[1] Jour. Chem. Soc. III, 354 (1847).

[2] Limmer: Das Ausbleichverfahren, 43 (1911).

[3] Koechlichen: Jour. Chem. Soc. *44*, 893 (1883).

coupier and induline require chromium or the latter mixed with magnesium acetate.

Of course, fastness to soaping is not the same thing as fastness to light; but the facts are suggestive and open up an unexplored field. Indigo is considered by the dyers as one of the most permanent dyes, while the painters consider it as fugitive.[1] "This rich and transparent blue is, unfortunately, gradually oxidized and browned, when exposed to light. In thin washes of water-color it disappears rapidly in the sun's rays, much more slowly when submitted to diffused daylight. The following figures approximately represent the reduction in force of a sample of indigo as a moist water-color when exposed to sunlight:

Original intensity	10
After two years	1
After ten years	0

Other trials with other samples gave in some cases less unfavorable results. Indigo in cake is sometimes less affected by sunlight than the moist preparations. As an oil-color, indigo loses from one-third to one-half its intensity when exposed to sunlight for five years, its hue being at the same time altered, in different specimens, either to a greyish or a greenish blue; the change is more conspicuous when the indigo has been mixed in tint with flake or other white. Locked up in a copal or amber varnish it is more slowly changed. The fading is due to oxidation."

Part of the difference in opinion between dyers and painters is probably due to differences in methods of testing; but I have a suspicion that oriental rugs owe part of their fastness to light to the fact that the weavers did not use chemically pure mordants.

If one wishes to study this subject experimentally, it is desirable to have a method by which tests can be made in a relatively short time. In another paper I report on some experiments along this line. By using different concentrations of peroxides or persulphates we can get oxidizing agents of different strengths in neutral, acid or alkaline solutions. By comparisons with dyes which are known to be fast to light we can lay down the arbitrary rule that a pigment is fast to light if there is no appreciable change

[1] Church: The Chemistry of Paints and Painting, 3rd Ed. 219 (1901).

in a given time in a given solution at a given temperature. Our experiments are only preliminary ones; but the method seems a promising one. There is one interesting thing to be noted. While we should expect to get the same bleaching by light and by the oxidizing agent, the rate of bleaching in the light varies with the relative intensity of the absorbed light, and the rates for any two lights are not necessarily equal when the relative intensities of the light are those necessary to make white light as we see it. As a matter of fact, we found that Victoria green bleaches more rapidly than eosine or methylene blue in a hydrogen peroxide solution while the reverse is the case in the sunlight.

There is another point about which we have no theory at present and that is as to the variation in stability with the method of preparation. Church[1] says that "vermilion prepared from mineral or native cinnabar is probably less liable to change than the artificial product, whether obtained by the dry way or the moist way, but moist way vermilions are certainly the most alterable." The artificial ultra-marine is more readily attacked by acids[2] and by alum than is lapis lazuli. So far as two samples of vermilion are mercuric sulphide they should behave alike. The difference must, therefore, be due either to agglomeration or to the presence of absorbed impurities. In either case it is a problem in colloid chemistry. Our general ignorance in regard to a lot of these things is illustrated by the fact that nobody knows whether lemon chrome and sublimed white lead are or are not definite compounds.

The general results of this paper:

1. Light may change pigments in all sorts of ways; but the change of color is usually due to an oxidation.
2. A drier in the oil may cause reduction of a pigment, the oil being oxidized; or it may accelerate the oxidation of the pigment.
3. Lead sulphide is oxidized to sulphate by light; and pictures which have blackened in the air can, therefore, be improved by an exposure to bright sunlight.
4. Colors which are really permanent may seem fugitive if prepared improperly or if ground in oil that has been bleached with acid.

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[1] Chemistry of Paint and Painting, 3rd Ed. 168 (1901).
[2] Toch: Materials for Permanent Painting, 163 (1911).

5. Madder probably protects vermilion by cutting off the rays which are most active in producing the allotropic change.

6. Varnishes keep out moisture, air, and ultra-violet light.

7. Pigments produced by oxidation are more likely to be stable than those produced by reduction.

8. By changing the nature of the precipitating agent it ought to be possible to vary the fastness of lakes to light.

9. From the analogy with dyeing, it seems probable that the maximum fastness to light can be obtained when lakes are made with a suitable mixture of precipitating agents.

10. It is doubtful whether copper salts increase the fastness of all dyes to light.

11. Rapid tests for fastness to light can be made with solutions of peroxides or of persulphates.

12. The relation between the stability of vermilion, etc., and the methods of preparation is a problem in colloid chemistry.

THE PHOTOCHEMICAL OXIDATION OF BENZENE

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In a paper published over thirty years ago, Leeds[1] showed that oxalic acid is formed and no phenol when benzene and moist phosphorus are allowed to stand in a warm place exposed to diffused light. If placed in full sunlight, considerable quantities of phenol are also formed. Ozone oxidizes benzene to oxalic acid, acetic acid, formic acid and carbon dioxide. Hydrogen peroxide oxidizes benzene to a mixture of oxalic acid and phenol, the relative amounts of phenol not being given. What really happens in Leeds' experiment is that moist phosphorus and air give rise to ozone in diffused light and to hydrogen peroxide in bright sunlight. He recognized this himself but he offered no explanation for the difference.

That the sunlight should have an effect is not surprising; but the problem is to determine why we should get hydrogen peroxide in the bright light and ozone in the diffused light. There is a rather remarkable paragraph in a paper by Wurster[2].

''Oxygen is made active and is converted in large amounts into the permanently active forms of ozone and hydrogen peroxide only when the rays of the sun fall upon oxygen and water simultaneously, as was first shown by Schönbein, though the fact was made use of for thousands of years in bleaching. Under these conditions of intimate contact of oxygen with drops of water, the oxygen is readily made active by light and the oxygen molecule is disrupted at ordinary temperature in a way which is otherwise obtained only at a very high temperature or under the action of a very intense lime light or electric light. The oxygen is split into atoms which react to form ozone and hydrogen peroxide. This is not so remarkable when we recall that, according to Graham, we must consider dissolved gases or gases con-

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[1] Ber. chem. Ges. Berlin, *14*, 975 (1881).
[2] Ibid., *19*, 3212 (1886).

densed on surfaces as being in the liquid state. They have therefore lost, as heat, the energy corresponding to the change to the liquid state; but, on the other hand, the readiness of the molecules to react is presumably increased by their being nearer together."

This would be admirable if Wurster had differentiated between the formation of ozone and hydrogen peroxide, instead of lumping the two together. The action of ordinary sunlight on a mixture of oxygen and water really forms hydrogen peroxide instead of ozone.

Wilson[1] has postulated the formation of hydrogen peroxide when ultra-violet light acts on moist oxygen. I quote from J. J. Thomson.[2] "Wilson showed that the passage of ultra-violet light through a gas (as distinct from the effects produced when it is incident on a metal surface) produces very interesting effects on the condensation of clouds. If the intensity of the light is small, then no clouds are produced unless the action equals that (1.25) required to produce clouds in gases exposed to Röntgen rays. If, however, the ultra-violet light is very intense, clouds are produced in air or in pure oxygen, but not in hydrogen, by very much smaller expansions, and the expansion required decreases as the time of exposure to the light increases; thus the nuclei producing the clouds grow under the influence of the light. If the light is exceedingly strong, clouds are produced in air or oxygen without any expansion at all. Wilson was even able to produce these clouds in air standing over a seventeen per cent solution of caustic potash, and which therefore was not saturated with water vapor; in this case the drops lasted for three hours after the light was cut off; this, as Wilson points out, shows that the drops cannot be pure water. These clouds are probably analogous to those observed years ago by Tyndall,[3] when ultra-violet light passes through air containing the vapors of certain substances of which amyl nitrite was the one which gave the most striking effects. The effects can be explained by the formation under the influence of the ultra-violet light of some substance—Wilson suggests that in his experiments it was H_2O_2 — which,

[1] Phil. Trans. *192*, 403 (1899).
[2] Conduction of Electricity through Gases, 2nd Ed. 169 (1900).
[3] Phil. Trans. *106*, 33 (1870).

by dissolving in the drops as they form, lowers the equilibrium vapor pressure, and thus enables the drops to grow under circumstances which would make drops of pure water evaporate. This explanation is supported by the fact that ultra-violet light does not produce these clouds in water vapor by itself or in hydrogen; and also by the fact that, unlike the clouds due to Röntgen rays, these clouds formed by ultra-violet light do not diminish in density when a strong electric field is applied to the gas, showing that the nuclei are either not charged or that if they are charged they are so loaded with foreign molecules that they do not move perceptibly in the electric field. Vincent[1] has observed movements of these drops in a strong electric field; he found that some drops moved in one direction, while there were some which did not move at all. Thus some drops are uncharged, others positively or negatively charged. It would thus seem that the charges have nothing to do with the formation of these drops, the drops merely forming a home for the ions produced by the ultra-violet light."

While these experiments make it probable that hydrogen peroxide is formed by the action of ultra-violet light on moist air, there is no direct proof of the presence of hydrogen peroxide and Vincent was not able to detect it. This gap has been filled by the experiments of Fischer and Ringe[2] who have shown that the silent discharge in an ozonizer produces hydrogen peroxide instead of ozone when the air is nearly saturated with water vapor. The failure to obtain ozone under these conditions is not surprising because it is a well-recognized fact in the commercial manufacture of ozone that the yield falls off unless the air is kept moderately dry. More recently Makowetsky[3] has shown that hydrogen peroxide is formed when a direct current glow discharge passes through oxygen or air to a water cathode. This is not an electrolytic phenomenon because the yield at low currents exceeds that called for by Faraday's law. It is just as much a photochemical reaction as is the ozone production. We should therefore expect to find that the action of sunlight on air would produce ozone when the air was moderately dry and when the

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[1] Proc. Camb. Phil. Soc. *12*, 305 (1904).
[2] Ber. chem. Ges. Berlin, *41*, 951 (1908).
[3] Zeit. Elektrochemie, *17*, 217 (1911).

sunlight was rich in ultra-violet light of wave-lengths less than 300. We should expect to get hydrogen peroxide in presence of water. The yield of ozone would of course be negligible in case the sunlight contained almost no rays having wave-lengths less than 300. The experiments of Bacon[1] offer a very satisfactory confirmation of this view. "When pure water or a salt solution is exposed to direct sunlight in Manila, hydrogen peroxide is formed very rapidly, strong tests being obtained after a few hours. H. D. Gibbs, of this Bureau, examined the solutions in a great number of reagent bottles exposed in the laboratory for some months to diffuse light and found considerable quantities of hydrogen peroxide in practically every case. It is evident that in the tropics, at least in island regions, with the great quantity of vegetable growth, the vigorous transpiration of plants, and the large amounts of water continually present at the surface of the earth and in the air, all the conditions are present when the sun is shining, which are necessary to charge the water surfaces, to form peroxide of hydrogen, and in general to increase the proportions of ions in the air according to the processes which have been outlined above. Whether there is a true ionization of the air by tropical sunlight, apart from such a secondary ionization, must be determined by further studies.[2] Considerable evidence is accumulating to show that the tropical sunlight contains more intense ultra-violet light than that in temperate zones. Thus I have shown in another paper[3] that the decomposition of oxalic acid or of oxalic acid catalysed by uranium salts is very much more rapid in the Philippines than in temperate zones, and Gibbs[4] has shown that the coloration of phenol and of aniline takes place much more rapidly in the tropics than in more northern zones.

"One of the most striking effects produced by ions is the influence they exert on the condensation of clouds. I have often noted, in watching a steam jet in the open air in Manila, the

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[1] Philippine Jour. Sci. *5* A, 271 (1910).

[2] In the Tenth Annual Report of the Director — the late Dr. Freer — it is stated that the ions have since been found to have been brought down from above.

[3] Philippine Jour. Sci. *5* A, 281 (1910).

[4] Ibid., *3* A, 361 (1909); *4* A, 133; *5* A, 9, 419 (1910).

remarkable way in which, as the sunlight strikes it, it becomes dense and beautifully colored, due to the interference and diffraction of the light by the small drops of water, while as soon as the sun goes behind a cloud, the jet becomes very thin, and the colors, of course, disappear. Other conditions being equal, on a cloudy day the mountains near Manila can be seen much more clearly than on one of sunshine, and I do not believe I err when I state that all days of bright sunshine in the Philippines show a decidedly hazy atmosphere, as noted by looking at objects at some distance. I believe this fact to be due to the ionization of the air by the sunlight and the consequent condensation of very minute drops of water around the ions so formed. The mountains are most clearly visible from Manila at sunrise and at sunset and on days when clouds protect the lower atmosphere from the ionizing radiations of the sun."

It does not seem very probable that the hydrogen peroxide in the reagent bottles in Manila could come from ionized air which got in when the bottles were opened. If this is not the case, oxygen and water must react to form hydrogen peroxide to some extent under the influence of light which can pass through glass.

The matter of the ionization of the air in Manila has been discussed by Freer[1] "Another phenomenon to be observed in Manila in a marked degree, and which, so far as I am aware, has not been recorded in the literature from other climates, is the extensive ionization of the air when exposed to the sunlight. Dr. Bacon, using a modern electroscope, has been able to show that our atmosphere, when exposed to the direct rays of the sun, rapidly discharges the instrument, the loss of potential being 46 volts per hour, whereas, in the diffused light of a room, it is only 15, and during the night 6, for the same volume of air. This is certainly a remarkable result, which deserves further study. The only comparative data on hand are a few by Elster and Geitel[2] giving us an indication of what the fall of voltage would be in northern climates. They found, in Vienna on a foggy day, a voltage of 2.77, in clear weather, 8.58, but on a day when the sky was half overcast, 13.67. These authors ascribe the phenom-

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[1] Philippine Jour. Sci. *5* B, 10 (1910).

[2] Drude's Ann. *2*, 425 (1900). The authors used an instrument of identical form with our own.

enon to radio-activity, but our results in Manila, where radioactive phenomena are not especially prominent, would lead to the conclusion that the air is ionized by sunlight. The presence of this ionization in so great a degree in our atmosphere would indicate a condition of the solar spectrum which might well account for many of the so-called excessive effects which have been observed."

Experiments were made in Manila to determine the extent of the solar spectrum at the ultra-violet end.[1] The spectra were obtained at noon. "They probably do not extend beyond $\lambda = 291\ \mu\mu$, and therefore not much farther than has been observed by others. Measurements undertaken by Miethe and Lehmann[2] in Assuan, Berlin, Zernatt, Gornergrat, and Monte Rosa give practically identical numbers, namely 291.55 $\mu\mu$ to 291.21 $\mu\mu$ during the latter part of August and the first part of September; these authors finding, in contradistinction to Cornu,[3] that altitude above the sea level makes no great difference. As one of these places is at 24° 30′ north latitude, while the others are in northern climates, it is evident that, as the extent of the ultraviolet field does not change materially, the intensity factor in the solar spectrum must vary to a great extent in different places. However, it is possible that a considerable range of ultra-violet is absent at present (March 1) from our sunlight. Probably this area will increase as the angle of the sun diminishes and as the season advances and it may reach a maximum in April, although these recent results would seem to indicate that even here we will not get below 288 $\mu\mu$."

These observations are important because they show that, under ordinary conditions, the sunlight reaching the earth contains practically none of the rays which cause the formation of ozone, the rays of wave-lengths less than 300 $\mu\mu$, while it does contain ultra-violet of wave-lengths greater than 300 $\mu\mu$, the rays which cause the decomposition of ozone. The bearing of this on our problem is easily shown. When phosphorus is oxidized, there is normally a production of ozone. In presence of

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[1] Freer: Philippine Jour. Sci. *5* B, 14 (1910).
[2] Sitzungsber. Akad. Wiss. Berlin, *8*, 268 (1909).
[3] Comptes rendus, *88*, 1107; *89*, 808 (1879).

benzene, we get the oxidation products characteristic of ozone — oxalic acid, etc., but no phenol. In bright sunlight the ultraviolet light actually present checks the formation of ozone by making it less stable. We consequently get a certain amount of hydrogen peroxide formed. The data are not sufficient to show whether the yield of ozone drops to zero. That would depend to some extent on the intensity of the sunlight. In presence of benzene we get the decomposition products characteristic of hydrogen peroxide or of a mixture of hydrogen peroxide and ozone, namely a mixture of phenol and oxalic acid.

It is not surprising that we should also get phenol when benzene, water, and palladium hydrogen are shaken up with air[1], because hydrogen peroxide is known to be a reduction product of oxygen.

The general results of this paper are:

1. When benzene is oxidized by ozone, the chief product is oxalic acid, while a mixture of oxalic acid and phenol is obtained when benzene is oxidized by hydrogen peroxide.
2. When moist phosphorus oxidizes in presence of benzene, the chief oxidation product of the benzene is oxalic acid when the reaction takes place in the dark or in diffused light. A mixture of oxalic acid and phenol is obtained if the reaction takes place in bright sunlight.
3. Hydrogen peroxide is formed by the action of the silent discharge, or of bright sunlight, upon a mixture of water and air.
4. At the surface of the earth bright sunlight rarely contains any appreciable amount of ultra-violet light having wavelengths less than 290 $\mu\mu$.
5. At the surface of the earth bright sunlight tends to destroy ozone and not to form it.
6. When moist phosphorus oxidizes in bright sunlight, the yield of ozone is decreased and that of hydrogen peroxide is increased.

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[1] Hoppe-Seyler: Ber. chem. Ges. Berlin, *12*, 1551 (1879).

THE SECOND POSITIVE

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During some preliminary work on solarization, we apparently obtained evidence of a second negative at relatively short exposures, followed by a second positive and a third negative. When this phenomenon was studied more carefully, it proved to be nonexistent. The trouble is due to the fact that, with long exposures, great differences occur between different boxes of the same make of plate; and there are also differences between plates in the same box.

The following stock solutions were used in all the work:

Solution A		Solution B	
Hydroquinone,	21g	Cryst. sodium carbonate,	252g
Cryst. sodium sulphite,	126g	Water,	1000g
Water,	1000g		

The developer consisted of one part Solution A, one part Solution B, and two parts water. In most cases development was carried on for one minute; but the time is given in all the tables. The plates were fixed in a twenty per cent hyposulphite solution.

TABLE I

Arc Light and Seed Lantern Slide Plates

Distance	Exposure	Development	Fixing	Result
30 ft.	½ min.	1 min.	3 min.	Negative
30 ft.	1 min.	1 min.	3 min.	Negative
30 cm.	1 sec.	1 min.	3 min.	Negative
30 cm.	3 sec.	1 min.	3 min.	Mongrel
30 cm.	½ min.	1 min.	3 min.	Good Positive
30 cm.	1 min.	1 min.	3 min.	Good Positive
30 cm.	12 min.	1 min.	3 min.	Poor Positive
30 cm.	25 min.	1 min.	3 min.	Poor Positive
30 cm.	90 min.	1 min.	3 min.	Very Poor Positive
30 cm.	100 min.	1 min.	3 min.	Very Poor Positive

In the first experiments an arc lamp was used as the source of light. The plates were Seed's Lantern Slide Plates. They were placed behind, and in contact with, a lantern slide at a fixed distance, usually 30 cm., and were exposed for varying times. The data are given in Table I.

From these data it was clear that excessive exposures would be necessary if one wished to get data on a second or third negative as the case might be. We therefore changed to Seed No. 30 plates. Some data with these plates are given in Table II.

TABLE II

Arc Light and Seed No. 30 Plates

Distance	Exposure	Development	Fixing	Result
30 cm.	1/4 sec.	1 min.	3 min.	Good Negative
30 cm.	1/2 sec.	1 min.	3 min.	Mongrel
30 cm.	3/2 sec.	1 min.	3 min.	Beautiful Positive
30 cm.	3 sec.	1 min.	5 min.	Positive
30 cm.	4 sec.	1 min.	3 min.	Negative
30 cm.	4 sec.	1 min.	3 min.	Positive
30 cm.	4 sec.	1 min.	5 min.	Positive
30 cm.	4 sec.	2 min.	5 min.	Positive
30 cm.	7 sec.	1 min.	3 min.	Positive
30 cm.	10 sec.	1 min.	3 min.	Negative
30 cm.	12 sec.	1 min.	3 min.	Positive
30 cm.	30 sec.	3/2 min.	5 min.	Fogged Positive
30 cm.	40 sec.	3/2 min.	5 min.	Fogged Positive
30 cm.	60 sec.	3/2 min.	5 min.	Fogged Positive
30 cm.	90 sec.	1 min.	3 min.	Fogged Positive
30 cm.	3.5 min.	3/2 min.	5 min.	Fogged Positive
30 cm.	5 min.	1 min.	3 min.	Cloudy Negative
30 cm.	6 min.	3/2 min.	3 min.	Fogged Positive
30 cm.	9 min.	1 min.	5 min.	Indistinct Negative
30 cm.	11 min.	1 min.	3 min.	Poor Negative
30 cm.	15 min.	2 min.	5 min.	Positive
30 cm.	60 min.	1 min.	3 min.	Fair Positive

In this Table we find positives and negatives galore but they are scattered round in a way which is anything but encouraging.

While it did not seem probable that the whole trouble could be due to the source of light, yet our 110-volt D. C. circuit is badly overloaded and the voltage fluctuates very much. Consequently a series of runs were made with exposure to a Welsbach burner. The data are given in Table III.

TABLE III

Welsbach Burner and Seed No. 30 Plates

Distance	Exposure	Development	Fixing	Result
30 cm.	10 sec.	2 min.	15 min.	Negative
30 cm.	30 sec.	2 min.	15 min.	Negative
30 cm.	75 sec.	2 min.	15 min.	Negative
30 cm.	4.5 min.	1 min.	5 min.	Positive
30 cm.	5 min.	1.5 min.	15 min.	Positive
30 cm.	6 min.	2 min.	15 min.	Mongrel
30 cm.	7.5 min.	2 min.	15 min.	Negative
30 cm.	8.5 min.	2 min.	15 min.	Negative
30 cm.	10 min.	1 min.	5 min.	Positive
30 cm.	20 min.	2 min.	15 min.	Positive
30 cm.	30 min.	1 min.	5 min.	Positive
30 cm.	45 min.	2 min.	15 min.	Positive
30 cm.	3 min.	2 min.	10 min.	Negative
30 cm.	4 min.	2 min.	10 min.	Negative
30 cm.	4 min.	2 min.	10 min.	Negative
30 cm.	5.5 min.	2 min.	10 min.	Negative
30 cm.	2 min.	1 min.	10 min.	Negative
30 cm.	5.75 min.	1 min.	10 min.	Negative
30 cm.	7.5 min.	1 min.	10 min.	Negative

The first series of measurements in Table III point to a first positive for exposures of about five minutes with a second negative at about eight minutes and a second positive at ten minutes. The next two series in Table III show no signs of a positive at about five minutes and consequently the negative at nearly eight minutes is still the first negative. The most plausible explanation seems to be variations in plates. The data in Tables IV and V are additional evidences of the difficulty of duplicating results.

TABLE IV

Welsbach Burner and Seed No. 30 Plates.

Distance	Exposure	Development	Fixing	Result
30 cm.	75 sec.	1 min.	15 min.	Negative
30 cm.	3 min.	1 min.	15 min.	Mongrel
30 cm.	4 min.	1 min.	15 min.	Negative
30 cm.	5 min.	1 min.	15 min.	Negative
30 cm.	7.5 min.	1 min.	15 min.	Positive
30 cm.	10 min.	1 min.	15 min.	Positive
30 cm.	12 min.	1 min.	15 min.	Positive
30 cm.	2.0 min.	1 min.	15 min.	Negative
30 cm.	2.5 min.	1 min.	15 min.	Negative
30 cm.	3.0 min.	1 min.	15 min.	Negative
30 cm.	3.5 min.	1 min.	15 min.	Negative
30 cm.	4.0 min.	2 min.	15 min.	Negative
30 cm.	4.5 min.	2 min.	15 min.	Negative
30 cm.	5.0 min.	2 min.	15 min.	Negative
30 cm.	5.5 min.	2 min.	15 min.	Negative
30 cm.	6.0 min.	2 min.	15 min.	Negative
30 cm.	6.5 min.	2 min.	15 min.	Mongrel
30 cm.	7.0 min.	2 min.	15 min.	Positive
30 cm.	10.0 min.	2 min.	15 min.	Positive

TABLE V

Welsbach Burner and Seed No. 30 Plates

Distance	Exposure	Development	Fixing	Result
30 cm.	6.5 min.	2 min.	15 min.	Negative
30 cm.	6.75 min.	2 min.	15 min.	Negative
30 cm.	7.0 min.	2 min.	15 min.	Mongrel
30 cm.	7.25 min.	2 min.	15 min.	Negative
30 cm.	7.5 min.	2 min.	15 min.	Mongrel
30 cm.	7.75 min.	2 min.	15 min.	Negative
30 cm.	8.0 min.	2 min.	15 min.	Mongrel
30 cm.	8.0 min.	2 min.	15 min.	Mongrel
30 cm.	8.5 min.	2 min.	15 min.	Mongrel
30 cm.	9.0 min.	2 min.	15 min.	Negative
30 cm.	9.5 min.	2 min.	15 min.	Negative

A striking feature of Table V is the occurrence of mongrels, which do not change into positives on slightly longer exposure. This could not be an effect due to the source of light because a deterioration of the Welsbach mantle would merely shove things along. We kept tab on the gas pressure and satisfied ourselves that the very slight fluctuations in pressure during the daytime could not be the cause of the trouble. This conclusion was confirmed by our getting normal, though different absolute, results in another run. With exposures up to 35 seconds we got a negative; with exposures of 45–60 seconds we obtained mongrels; with exposures of 1.25–30.0 minutes we obtained positives. In still another run, positives were not obtained until exposures exceeded two minutes and we were still getting positives after an exposure of an hour.

The most plausible explanation for the erratic results is that we are dealing with plates in which the silver bromide grains do not all have the same sensitiveness. Suppose that our plates contain a fast emulsion mixed with more or less of a slow emulsion. The two sets of grains will solarize at different exposures and the actual blackening will be the sum of the blackenings for the two single emulsions. It is easy to see that the curves for the two single emulsions might be such that they gave an additional maximum in the combined curve or changed things so that a positive could not be obtained when copying a lantern slide having a wide range of densities.

Although efforts were made to keep track of the conditions of development, there was always the possibility of a slight, unknown variation in the conditions. It was therefore decided to develop a number of plates simultaneously in a plate tank. For this we used Eastman's developer for 4 x 5 plates and developed in 36 oz. of solution at 65° F. for twenty minutes, fixing in a hyposulphite bath and washing thoroughly in cold water. Instead of being exposed behind a lantern shade, the plates were placed in a plate holder and the slide withdrawn to such an extent as to give five different exposures on the same plate. The following results were obtained.

I. Strips exposed 1/5, 3/5, 5/5, 7/5, 9/5 seconds. The density increases with increasing exposure.

II. Strips exposed 20, 40, 60, 80, 100 seconds. The density increases with increasing exposure.

III. Strips exposed 110, 115, 120, 125, 130 seconds. Apparently one flat tone; cannot distinguish strips. Density same as 100 seconds exposure in II.

IV. Strips exposed 135, 140, 145, 150, 155 seconds. Apparently one flat tone; same as III.

V. Strips exposed 3, 6, 9, 12, 15 minutes. Density decreases with increasing exposure. First strip (3 min.) same density as IV.

VI. Strips exposed 15, 30, 45, 60, 75 minutes. Density decreases with increasing exposure up to 45 min; density of the fourth strip (60 min.) same as that of third strip and less than that of fifth strip.

VII. Strips exposed 3, 4, 5, 6, 7 minutes. Density decreases with increasing exposure.

VIII. Strips exposed 8, 9, 10, 11, 12 minutes. Density decreases with increasing exposure. VII and VIII duplicate V very well.

IX. Strips exposed 13, 14, 15, 16, 17 minutes. Apparently one flat tone.

X. Strips exposed 18, 19, 20, 21, 22 minutes. Apparently one flat tone; same as IX.

XI. Strips exposed 25, 27, 29, 31, 33 minutes. Apparently one flat tone; same as X.

XII. Strips exposed 35, 37, 39, 41, 43 minutes. Flat; same as IX–XI.

XIII. Strips exposed 15, 30, 45, 60, 75 minutes. Density decreases with increasing exposure for first three strips; density of last three strips practically the same, though last strip may be a little the darkest.

XIV. Strips exposed 50, 55, 60, 65, 70 minutes. Apparently one flat tone.

XV. Strips exposed 2, 4, 6, 8, 10 minutes. Decreasing density with increasing exposure.

XVI. Strips exposed 1/2, 3/2, 5/2, 7/2, 9/2 minutes. Decreasing density with increasing exposure. Does not agree well with II and III.

XVII. Strips exposed 3, 30, 70, 110, 150 minutes. Decreasing density with increasing exposure for first four strips. Last strip (150 min.) darker than fourth strip.

These experiments seem to show that the strips increase rapidly in density as the exposures increase from 0.2 second to 1.8 seconds; that the density increases gradually as the exposure increases from 1.8 seconds to 100 seconds. With exposures varying from two to three minutes there is only a very slight change in density. There is a slow decrease in density as the exposures increase from three minutes to twelve minutes, and practically no change in density with exposures increasing from twelve minutes to seventy minutes. These conclusions are based on qualitative measurements. That there is a decreasing density with exposures increasing from three minutes to one hundred and ten minutes appears from XVII where the intervals are sufficiently large to be detected by the unaided eye. If we compare XVII with VI, we see the marked effect due to the individual plate, the second negative beginning at over 110 minutes in one case and at about 60 minutes in the other case.

The general results of this paper are:

1. If a second positive exists, it requires a very long exposure even with a very bright light.
2. In many cases a false first positive or a false mongrel may be obtained.
3. Since the emulsion on an ordinary plate is probably never homogeneous, one really observes a combination solarization curve.
4. The inhomogeneity of the emulsion may easily be the cause of the false first positives or of the false mongrels.
5. With long exposures we find great differences between different boxes of the same make of plates and we even find some differences between the plates in the same box.

RAPID TESTING OF DYES AND PIGMENTS

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The actual testing of dyes and pigments in regard to their relative permanency to light is slow work. Of course the time can be cut down somewhat by using a very intense source of light; but this is permissible only in case one is certain that the amount of change is proportional to the product of the intensity of light into the time of exposure. There is no certainty that that is true in any particular case even when using monochromatic light and it certainly is not the case with an arc light. In fact the whole nature of the reaction may change. Methylene blue may be oxidized or reduced. In the immediate neighborhood of a quartz, mercury vapor, lamp, there is enough ozone formed to bleach colors which would ordinarily be perfectly stable.

Since most colors are bleached by oxidation, it seemed that it ought to be possible to prepare solutions of oxidizing agents of varying strengths such that one could say that a given dye or pigment was practically fast to light in case it did not bleach perceptibly in a given solution within a given time. Our experiments are only preliminary ones; but they indicate the possibility of working out a satisfactory method along these lines.

Experiments were first made with methylene blue, methyl violet, Victoria green, magenta, azo red, and eosine, using hydrogen peroxide as oxidizing agent. The concentration of the dyes was 0.1g per liter. In the first series, 0, 2, 4, 8, 10 cc. of a three per cent solution of hydrogen peroxide were added respectively to bottles each containing 10 cc. of the dye solution. The thirty-six bottles were shaken and then put away in the dark. They were examined every day for about four weeks. The following results were obtained at the end of twenty-seven days:

Methylene blue

All bottles containing hydrogen peroxide have faded as compared with the standard; not very much difference owing to concentration of hydrogen peroxide, though the shade gets a little lighter as the concentration increases.

Methyl violet

The bottles containing 2 and 4 cc. hydrogen peroxide solution are much lighter than the standard; but the two are apparently exactly alike. With increasing concentration of H_2O_2, the color decreases rapidly, the 10 cc. bottle being practically colorless.

Victoria green

The bottle with 2 cc. H_2O_2 solution shows a slight tinge of green; the other bottles are quite colorless. The dye is much more fugitive to hydrogen peroxide than methylene blue or methyl violet.

Magenta

The 8 cc. and 10 cc. bottles are entirely faded; the others have a slight color, the 2 cc. bottle having a little the most color.

Azo red

There is a slight pink tinge in the bottle containing 2 cc. H_2O_2; but the others are almost colorless.

Eosine

Not much change in the 2, 4 and 6 cc. bottles. The other two are almost colorless.

The objection to these tests is that the concentration of the dye varies in the ratio of one to two and this might be considered as objectionable. In order to eliminate this, a series of experiments was made in which 1 cc. of the dye solution (0.1g per liter) was taken in every case. We added 50 cc., 35 cc. and 25 cc. of the three per cent solution of hydrogen peroxide to different bottles and diluted all solutions to 51 cc. The solutions were examined at the end of 16, 41, and 65 hours; in other words, on each of the next three days.

Methylene blue

After 16 hours no very great change as compared with the standard, though the 50 cc. and 35 cc. bottles are a bit faded, the shade being greenish rather than bluish. After 41 hours all three solutions are distinctly faded, the change being more marked with the 35 cc. and 50 cc. bottle than with the 25 cc. one. After 65 hours the results are about the same as after 41 hours.

Methyl violet

After 16 hours all three solutions have faded considerably, and there is a regular gradation, the solution containing the most H_2O_2 having faded the most. After 41 hours the 50 cc. bottle is entirely colorless; the 35 cc. bottle has a very slight tinge of color and the 25 cc. bottle a slight tinge. After 65 hours all three solutions are almost entirely faded.

Victoria green

After 16 hours the 50 cc. bottle has only a very slight greenish tinge. The other two bottles have apparently faded about equally but not quite so much as the 50 cc. bottle. After 41 hours the color is entirely gone in all three bottles.

Magenta

After 16 hours the 50 cc. bottle shows almost no color; the 35 cc. bottle shows a little more color; and the 25 cc. bottle is distinctly colored, though very much faded as compared with the standard. After 41 hours there is no color in any of the bottles.

Azo red

After 16 hours all three bottles are distinctly faded; but the differences among themselves are less than the difference between them and the standard. After 41 hours the three bottles have about the same tint. Though very much faded, there is still color. After 65 hours there is still a trace of color in all three bottles.

Eosine

After 16 hours all three bottles have a distinctly yellower color than the standard. The 50 cc. and the 35 cc. bottles have faded about equally and quite a bit more than the 25 cc. bottle. After 41 hours the 50 cc. and the 35 cc. bottles are almost entirely faded and the 25 cc. bottle is pretty far gone. After 65 hours the 50 cc. and the 35 cc. bottles are entirely faded and there is only a slight color in the 25 cc. bottle.

These experiments show that it is possible to distinguish quite sharply between these dyes. Methylene blue is distinctly the most stable to hydrogen peroxide; next comes azo red; and then come methyl violet and eosine; while Victoria green and magenta are the most fugitive under these circumstances. As has been stated, these experiments are only preliminary ones and will have to be extended so as to cover some of the more stable dyes. As far as they go, they are distinctly encouraging.

The difference in the dyes can be shown in another way, the results being a first approximation only and varying of course with the temperature. Starting with 1 cc. dye solution (0.1g per liter) and 50 cc. three per cent hydrogen peroxide solution, the time necessary for fading was 20 hours for magenta (completely faded); 23 hours for Victoria green (completely faded); 48 hours for eosine (almost entirely faded); 65 hours for methyl violet (almost entirely faded); 95 hours for azo red (completely faded); while methylene blue was still standing up at the end of 200 hours.

Experiments were next tried with some lake colors presented to us very kindly by Messrs. Toch Brothers of New York. The names and descriptions of these colors were as follows:

Eosine vermilion: an eosine precipitated with lead acetate on red lead (orange mineral).

Scarlet lake: 2 R Scarlet fastened with barium chloride on barium sulphate and alumina hydrate.

Ian red: an azo cerise on blanc fixe.

Red lake, No. 625: an azo red on barium sulphate and clay.

Eosine lake, No. 1812: eosine fastened with lead acetate on alumina hydrate and barium sulphate.

Magenta lake, No. 678: magenta on alumina hydrate.

Blue mauve, No. 676: methylene violet on alumina hydrate.

Green lake deep: Victoria green and methylene blue on clay.

Green lake yellow: Victoria green and auramine on clay.

In these experiments we weighed out 0.05g of the pigment, added it to 60 cc. H_2O_2, shook for two minutes in a mechanical shaker, and then put the bottle away in the dark for six days. The solutions were filtered, the pigments dried and compared with the original color. In some of the cases the lakes had bled considerably.

Eosine vermilion

Bleeds slightly more than eosine lake and fades more. The standard is much darker than the sample which has been treated with hydrogen peroxide.

Scarlet lake

Bleeds very noticeably. After treatment with hydrogen peroxide the color changes from scarlet to orange red.

Ian red

Bleeds very badly and fades very much, turning to a pale pink color.

Red lake

Bleeds much and turns to a pale orange color.

Eosine lake

Bleeds slightly; but not so much as eosine vermilion. Fades a good deal, the color becoming more of an orange.

Magenta lake

Bleeds scarcely at all but fades almost completely, though there is a faint color left.

Blue mauve

Not much bleeding. Fades considerably, changing from a dark purple color to a light pale lavender.

Green lakes

Practically no bleeding. Fade very much, turning to a grayish green color

Since it was possible that the change of color was due in large part to the bleeding and not to the bleaching, the preceding experiments were repeated, substituting 60 cc. H_2O for 60 cc. H_2O_2 solution. Though all the lakes, except the greens, bled noticeably, the colors of the filtered and dried lakes were practically those of the original samples, showing that very little actual color had been washed out and that hydrogen peroxide did actually cause the lakes to fade. It is to be noticed that these lake colors resist the action of hydrogen peroxide very much better than did the corresponding dyes.

Some experiments on the dyes previously studied showed that potassium persulphate acted more rapidly than hydrogen peroxide of the concentration we were using. Experiments were also made with a number of other dyes. The solutions were made up to contain 0.03g dye, 7g $K_2S_2O_8$ and 80 cc. H_2O. The approximate times for practically complete fading were 16 hours for naphthalene red; 19 hours for rosazarine; 23 hours for neutral violet extra; 25 hours for naphthalene yellow; 36 hours for Rose Bengale; 58 hours for azo acid violet 4 R; 60 hours for Victoria violet; 60 hours for cotton orange; 238 hours for diamine fast yellow; and 250 hours for diamine gold.

One run was made with the lakes at 60°–75°, the solution consisting of 0.05g pigment, 7g $K_2S_2O_8$, and 80 cc. H_2O as before. The approximate times for complete fading were about 10 hours for blue mauve; 15 hours for eosine vermilion and red lake; 48 hours for scarlet lake; 53 hours for eosine lake; 90 hours for green lake deep; while Ian red did not become entirely colorless in 150 hours. These results are not entirely in accord with those obtained with hydrogen peroxide at ordinary temperature. It is an open question whether the time necessary for complete bleaching is a satisfactory criterion in the case of the lakes. Most of the lakes bleach very much in the first hour or so and then change very slowly. Probably a measure of the percentage change in a moderately short time would be more satisfactory.

Experiments were next made as to the bleaching action of sunlight on dyes in solution, using the same six dyes which were tested with hydrogen peroxide. To 10 cc. of the dye solution (0.1g per liter) there were added 40 cc. H_2O. Owing to the unsettled weather no absolute measure of the time of fading could be obtained; but eosine bleached the most rapidly and then methylene blue. In course of time the methyl violet, magenta, Victoria green and azo red solutions all bleached to colorless liquids. This is in keeping with the experiments showing that all these dyes bleach in presence of hydrogen peroxide. There is a discrepancy in that eosine and methylene blue are the first to fade in the sunlight, whereas methylene blue is the last to fade in hydrogen peroxide. This is a bit puzzling; but, after all, it is really no more surprising than that one reaction should go faster than another in one solvent and slower in another. Both are beyond us for the present. The practical bearing of it is that we may use the hydrogen peroxide test, within certain limits, to show stability of a given dye to light; but we must not use it to measure relative rates of fading on exposure to light. It is not necessarily light of the same wavelength which acts on any two of the dyes and the results will therefore vary among themselves with the varying nature of the source of light. Thus eosine fades relatively faster than methylene blue when exposed to the light of a quartz, mercury vapor, lamp and both gain relatively to the other four dyes under these circumstances. When using the standard solution of 0.05g per liter, the time for practically complete fading is about 5 hours for eosine; 8 hours for methylene blue; 15 hours for methylene violet; 20 hours for azo red and for magenta, while Victoria green takes about 24 hours to bleach. On standing in the dark the color comes back with the methylene blue and to some extent with the others.

Experiments were next made with 0.03g of each lake suspended in 80 cc. water. The mixtures were exposed to sunlight for seven weeks and were examined daily. Only about 13 or 14 days out of the lot were really bright days. The eosine faded first, and then the eosine vermilion which did not go completely. The scarlet lake was next to go and then came blue mauve and magenta lake, none of these three becoming entirely colorless. The red lake faded slightly while the greens were not changed much and the Ian red showed no change of color that we could detect.

The dry, powdered, lakes were exposed to sunlight, such as it was, for about six weeks. During this time the eosine was the only one to fade noticeably.

Reference has been made to the possible desirability of determining the percentage bleaching at the end of the given time instead of noting the time necessary for complete fading. The relative results will not be the same by the two methods unless the time-color curves are of the same general shape. While we have no quantitative data on this point, we made a few qualitative experiments along this line with hydrogen peroxide as oxidizing agent. Methylene blue and azo red fade gradually, the azo red fading faster than the methylene blue. Methyl violet and eosine fade very little at first, standing up almost as well as methylene blue; then they suddenly fade very fast. Magenta and Victoria green fade very fast at first and then very gradually. For short intervals of time, methyl violet and eosine are apparently more stable than azo red, while the reverse is true for longer intervals.

The general results of this paper are:

1. Methylene blue, methyl violet, Victoria green, magenta, azo red, and eosine are bleached at ordinary temperature by a suitable concentration of hydrogen peroxide. It is easy to arrange the experiment so as to bring out marked differences in the relative stability of these dyes.
2. Methylene blue and azo red fade gradually; methyl violet and eosine fade slowly at first and then quite rapidly; magenta and Victoria green fade fast at first and then gradually.
3. Taking practically complete bleaching as the endpoint, the order of stability is methylene blue, azo red, methyl violet, eosine, Victoria green, and magenta, the last being the most fugitive. For shorter intervals of time the order may be methylene blue, methyl violet, eosine, azo red, Victoria green, and magenta.
4. A similar bleaching effect can be obtained with persulphate solutions.
5. Solutions of all six dyes bleach in the sunlight and also in the light of the quartz, mercury vapor, lamp. The order of stability is not the same as in the oxidizing solutions, being Victoria green, magenta and azo red, methyl violet, methylene blue, and eosine, the last being the most fugitive. This discrepancy is due in part to the fact that the oxidation of the dyes is not always due to light of the same wave-length.
6. We have studied the action of hydrogen peroxide and of sunlight on the following lake colors: eosine vermilion, scarlet lake, Ian red, red lake, eosine lake, magenta lake, blue mauve, green lake deep, green lake yellowish.
7. All the lakes, except the greens, bled badly and all were bleached very much by hydrogen peroxide. They are very much more stable to hydrogen peroxide and to sunlight than the corresponding dyes.

8. The dry lakes were not much affected by six weeks' exposure to occasional sunlight, the eosine fading much the most.

9. When suspended in water, the lakes are bleached by sunlight, the order of permanency under the conditions of the experiment being Ian red, the greens, red lake, magenta lake and blue mauve, scarlet lake, eosine vermilion, and eosine lake, the last being the most fugitive.

10. These preliminary results indicate the possibility of working out rapid qualitative tests as to the stability of dyes and pigments in sunlight. Such tests are absolutely necessary for any systematic study of the factors affecting stability.

THE SILVER EQUIVALENT OF HYDROQUINONE

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One molecular weight of hydroquinone is said by Andresen to reduce two molecular weights of silver bromide when no sulphite is present[1] and four molecular weights when sulphite is present.[2] The actual figures given by Andresen work out about 4.38 instead of 4; but that is of no importance at present. Reeb[3] dissolved silver oxide in ten per cent sodium sulphite solution and found that one molecular weight of hydroquinone precipitated eight molecular weights of silver. We apparently have the following results:

1 M Hydroquinone = 2 M Ag (AgBr)
1 M Hydroquinone = 4 M Ag (AgBr and Na_2SO_3)
1 M Hydroquinone = 8 M Ag (Ag_2O dissolved in Na_2SO_3).

This is bad enough; but Mees and Sheppard[4] go one step farther. They consider that hydroquinone reacts with silver bromide in presence of alkalies according to the equation,

$$C_6H_4(O\ K)_2 + 2\ AgBr = 2\ Ag + C_6H_4O_2 + 2KBr.$$

In presence of an excess of alkali, the quinone forms the potassium salt of hydroquinone, and hydrogen peroxide,

$$C_0H_4O_2 + 2KOH = C_6H_4(O\ K)_2 + H_2O_2.$$

Since both hydroquinone and hydrogen peroxide reduce silver bromide in alkaline solution, there is no apparent reason why these changes should not go on forever and why a given amount of hydroquinone should not reduce an indefinite amount of silver bromide. A fair statement of Mees's view would be that, in

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[1] Eder's Handbuch der Photographie, 5th Ed. *3*, 312 (1903).
[2] Namias: Chimie photographique, 264 (1902).
[3] Reiss: Die Entwickelung der photographischen Bromsilbertrockenplatte und die Entwickler, 30 (1902).
[4] Zeit. Wiss. Photographie, *2*, 9 (1904).

the absence of air, a solution of hydroquinone containing an excess of sulphite and of alkali would reduce any amount of silver bromide, were it not for side reactions which probably occur.

Under the circumstances it seemed as though more experiments were desirable. The silver bromide was prepared by precipitation from a solution of silver nitrate with a slight excess of potassium bromide. The precipitate was washed until the wash water was free from soluble bromides; it was then dried at 110°, ground and sifted through a 40-mesh sieve. No special care was taken to protect the silver bromide from diffused light because the amount of decomposition due to this cause falls way inside the limits of experimental error. A given amount of alkaline hydroquinone solution was allowed to react with an excess of silver bromide for a given time. The solution was then filtered through a Gooch crucible and the silver-coated silver bromide was washed with water to which a little potassium sulphate was added in case the silver or the silver bromide showed any tendency to go into colloidal suspension. The potassium sulphate coagulated any suspended silver or silver bromide. When the washing was completed, the silver bromide and the asbestos of the Gooch crucible were treated with 1: 1 nitric acid The dissolved silver was then titrated with N/2 NH_4SCN, using ferric alum as indicator.

The first runs were made to determine the conditions affecting the reaction between silver bromide and hydroquinone. A very few experiments showed that stirring or shaking was essential if complete reduction was to be obtained. This is not surprising because we are dealing with a reaction in a heterogeneous system and consequently rate of diffusion would naturally be an important factor. The machine, which was used to keep the solutions stirred, consisted of a reduction gear run by an electric motor. The reduction gear was fitted with a face-plate which was rotated at the reduced speed. A wooden disc was bolted to this face-plate and the bottles (of about 25–30 cc. capacity and closed with rubber stoppers) containing the solution and silver bromide were fastened to the outer edge of the disc. As this disc revolved, the contents of the bottles were kept stirred by the silver bromide falling from one end of the bottle to the other.[1]

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[1] Special experiments showed that the small volume of air left in the bottles did not introduce any serious error.

The experiments in Table I show how necessary stirring is.

TABLE I

Hydroquinone 0.11g, NaOH 2.2g, in 25 cc.
Excess of AgBr. Temperature, ca 20°

Conditions	Time	Mols Ag reduced per Mol Hydroquinone
Not shaken at all	1 day	4.19
	2 days	4.13
	3 days	4.76
Shaken by hand	3 days	5.48
	3 days	5.20
	3 days	5.16
Shaken by machine	6 hours	6.38
	6 hours	6.38
	6 hours	6.58

Experiments on the effect of temperature are given in Table II. In these runs the bottles were shaken occasionally by hand. They show the effect just as well as though the shaking had been done by machine and consequently it did not seem worth while to make a thermostat with a rotating device for this work.

TABLE II

Hydroquinone 0.11g, NaOH 2.2g, in 25 cc.
Excess of AgBr. Shaken by hand

Temperature	Time	Mol Ag reduced per Mol Hydroquinone
ca 20	6 hours	5.69
65°–70°	30 mins.	8.0
95°–100°	6 hours	9.29

From these experiments it is clear that the reaction velocity increases rapidly with rising temperature.

A few experiments were made to determine whether light had any marked effect on the reaction. The data are given in Table III.

TABLE III

A. Hydroquinone 0.11g, NaOH 2.2g, in 25 cc.
B. Hydroquinone 0.055g, NaOH 2.2g, in 25 cc.
Excess of AgBr. Temperature, ca 20°.

Sol.	Conditions	Mol Ag reduced per Mol Hydroquinone
A	Solution exposed only to diffused light	5.84
A	Solution exposed to sunlight	5.69
B	AgBr not exposed	6.05
B	AgBr blackened by light	6.05

The two sets are not comparable one with another; but the two experiments with solution A are comparable and so are the two experiments with solution B. Light has little, if any, effect on the reaction. It is not claimed that equilibrium was reached in these experiments.

The experiments in Table IV show the effect of alkali on the rate.

TABLE IV

Hydroquinone 0.055g, alkali variable, in 25 cc.
Excess of AgBr. Temperature, ca 20°

Approx Mol Alkali per Mol Hydroquinone	Mol Ag reduced per Mol Hydroquinone
10 Mol Na_2CO_3	3.8
10 Mol NaOH	5.5
100 Mol NaOH	6.4

The rate increases with increasing concentration of alkali. In all experiments a large excess of alkali was used.

Several runs were made to get some idea of how soon equilibrium is reached. In all of these runs a little fresh AgBr was added once or twice daily so as to be certain that there should always be a comparatively clean surface of silver bromide exposed to the hydroquinone solution. The results are given in Table V.

TABLE V

Hydroquinone 0.11g, NaOH 2.2g, in 25 cc.
Excess of AgBr. Temperature, ca 20°

Time	Mol Ag reduced per Mol Hydroquinone
6 hours	6.38
6 hours	6.58
8 days	7.8
15 days	7.95
18 days	8.06

Equilibrium has not certainly been reached even at the end of eighteen days. From this experiment and from experiments covering shorter lengths of time, it seems probable that the reaction goes in at least two stages. In the first stage about six molecular weights of silver are reduced in a short time, while the second stage requires a much longer time, equilibrium not having been reached definitely in eighteen days. At 100° more than nine molecular weights of silver were reduced in six hours even though the stirring was less efficient. Of course, there is no certainty that the endpoint is the same at 100° as at 20°. It may easily be that the reaction runs farther at the higher temperature.

Since quinone is presumably one of the oxidation products of hydroquinone, it seemed desirable to determine the silver equivalent of quinone under similar conditions. The data are given in Table VI.

TABLE VI

A. Hydroquinone 0.11g, NaOH 2.2g, in 25cc.
B. Quinone 0.108g, NaOH 2.2g, in 25 cc.
Excess of Ag Br. Temperature, ca 20°

Sol.	Reducing Agent	Mol Ag per Mol Reducing Agent
B	Quinone	4.70
B	Quinone	4.85
A	Hydroquinone	6.38
A	Hydroquinone	6.58

From these experiments it appears that hydroquinone reduces nearly two more molecular weights of silver bromide than does quinone while theory calls for a difference of exactly two provided equilibrium is reached. These experiments make it reasonably certain that the quinone is an intermediate product when hydroquinone reduces silver bromide. It is also very improbable that there is any regeneration of hydroquinone under these conditions.

In Table VII are given data for the silver equivalent of hydroquinone in presence of sodium sulphite.

TABLE VII

Hydroquinone 0.055g, NaOH 2.2g, in 25cc.
Excess of AgBr. Temperature, ca 20°
M. S. = Mol Sulphite per Mol Hydroquinone
M. Ag = Mol Ag reduced per Mol Hydroquinone

Time	M. S.	M. Ag	Time	M. S.	M. Ag
4.5 hours	0	6.2	18 days	0	7.63
4.5 hours	2	7.95	18 days	0	7.68
4.5 hours	5	8.25	18 days	1	7.76
4.5 hours	15	8.15	18 days	1	7.68
4.5 hours	0	6.4	18 days	5	8.4
4.5 hours	5	8.4	18 days	10	8.94
4.5 hours	10	8.38	18 days	10	8.94

When sulphite is present, the silver equivalent is only a little higher at the end of 18 days than it is at the end of 4.5 hours, thus showing that at any rate the first stage of the reaction takes place fairly rapidly. For runs of 4.5 hours about two more molecular weights of silver are reduced when sulphite is present in excess than without it. On the eighteen days' run this difference drops to about one molecular weight of silver. Since this change is due to an increase in the silver equivalent when no sulphite is present, it is probable that the reaction proceeds along different lines when sulphite is present. In the short runs the silver equivalent is practically the same for amounts of sulphite varying from five to fifteen molecular weights per molecular weight of hydroquinone.

In order to determine whether the increased silver equivalent in presence of sulphite was due to an oxidation of the sulphite or to an increased reducing action of the hydroquinone, a determination was made of the amount of sulphite left in the solution. After the reaction had been allowed to run as long as wished, the solution was poured through a Gooch filter and the mixture of silver bromide and silver was washed. The filtrate was transferred to a small round-bottomed flask of about 150 cc. capacity, which was fitted with a separatory funnel and with a glass tube which led to a series of two U-tubes containing half normal iodine solution. To the solution in the flask was added about 15 cc. conc. sulphuric acid containing sufficient silver sulphate to react with any hydrobromic acid set free on acidifying. After all the acid had been added, carbon dioxide was run through the apparatus and the flask was heated to drive off all the sulphur dioxide, which was then taken up by the half-normal iodide solution in the U-tubes. A third U-tube, containing potassium iodide solution, was placed at the end of the series to take up any iodine which might be volatilized and driven over from the other two tubes. The amount of sulphite could be determined from the change in the titre of the iodine solution. This method of analysis is not very accurate but the data in Table VIII seem to show that one molecular weight of sulphite has been oxidized and that the extra two molecular weights of silver are due to this cause.

TABLE VIII

Conditions	Mol Sulphite taken	Mol Sulphite oxidized
Blank	3.82	0.0
AgBr	2.52	1.30
AgBr	2.78	1.04

Since the amount of sulphite oxidized does not increase when the molecular ratio of sulphite to hydroquinone increases from 5 to 15, it is evident that the direct reduction of silver bromide by sodium sulphite is small under the conditions of the experiment and that we must be dealing with a coupled reaction of some sort. Some experiments were made to show that the coupling takes place with hydroquinone and with quinone rather than with any of the oxidation products of quinone. The data for hydroquinone are given in Table IX.

TABLE IX

Hydroquinone 0.055g, NaOH 2.2g, in 25 cc.
Excess of AgBr. Temperature, ca 20°
Time of run, 3 hours.

Mol Sulphite per Mol Hydroquinone	Conditions	Mol Ag reduced per Mol Hydroquinone
0	———	6.3
10	Sulphite added before run	8.05
10	Sulphite added 5 minutes after run started	7.2
10	Sulphite added 15 minutes before run ended	6.3

When the sulphite is added toward the end of the run it has practically no effect; when it is added before the run, the silver equivalent is increased by nearly 2; when the sulphite is added just after the run has started the silver equivalent is increased by about 1. The increase of about one in the silver equivalent when the sulphite is added just after the run begins, might be a coincidence due to the hydroquinone being partially oxidized; but the data in Table X rather imply that the oxidation to quinone takes place very rapidly and that we are really dealing with quinone.

TABLE X

Quinone 0.054g, NaOH 2.2g, in 25 cc.
Excess of AgBr. Temperature, ca 20°

Time	Mol Sulphite per Mol Hydroquinone	Mol Ag reduced per Mol Hydroquinone
1 hour	0	3.9
1 hour	5	4.9
1 hour	10	4.95

Under these conditions we get one more molecular weight of silver reduced in presence of an excess of sodium sulphite. The induced reaction apparently takes place in two stages, one-half molecular weight of sodium sulphite being oxidized while one molecular weight of hydroquinone is being oxidized to quinone, and the other half molecular weight of sodium sulphite being oxidized while quinone is being oxidized to something else. It would have been interesting to study this further as a case of an induced reaction; but that would have been entirely outside the scope of this present paper.

A few experiments were also made to determine the silver equivalent of hydroquinone with other silver salts than the bromide. The data are given in Tables XI.

TABLE XI

Hydroquinone 0.55g, 20 cc. NH_4OH (sp. g. 0.90), and variable $AgNO_3$, in 40 cc. solution. Temperature, ca 20°.

Time	$AgNO_3$ grams	Mol Ag reduced per Mol Hydroquinone
5 mins.	0.85	5.11
5 mins.	1.7	6.67
2 days	1.7	6.82
8 days	1.7	8.03

Silver Sulphite 1.87g, Sodium Sulphite 3.78g, Hydroquinone 0.055g, NaOH 2.2g, in 40 cc. Temperature ca 20°.

Time	Mol Ag reduced per Mol Hydroquinone
5 mins.	8.2

Hydroquinone 0.055g, NaOH 2.2g, in 25 cc.
Excess of Ag_2O. Temperature, ca 20°

Time	Mol Ag reduced per Mol Hydroquinone
5 mins.	10.4
15 hours	10.5

The reaction apparently takes place very rapidly with silver oxide and alkali, and the silver equivalent is very high, being higher in five minutes than that obtained for silver bromide after heating at 100° for six hours. The reaction is also very rapid with silver sulphite dissolved in sodium sulphite, an equivalent of about 8 being obtained in five minutes. No attempt was made to determine the equilibrium and no measurements were made as to the amount of sulphite oxidized. It is probable that the same relations hold as in the case of silver bromide and sodium sulphite. With ammoniacal silver nitrate a silver equivalent of nearly 7 is reached very rapidly and this creeps up to about 8 in the course of about as many days.

In relatively few of the experiments are the silver equivalents integers. The variations may be due in some cases to experimental error; but that is undoubtedly not the explanation in all cases. There are two other ways, besides experimental error, in which a reaction taking place according to definite proportions may appear not to. We may be dealing with a reaction which does not run to an end or we may have the reducing agent oxidized in two or more different ways in which case we should be measuring the sum of two reactions, neither of which perhaps runs to an end. Theoretically the reactions do not run to an end because the reducing power of the solution varies with the concentration. It is quite probable, however, that the effect due to this is negligible. In view of the difficulty of coming out with only one product when making organic preparations, it is very improbable that the oxidation of hydroquinone proceeds along one line only. This view is confirmed by the fact that the silver equivalent of hydroquinone is about eight on long runs (Cf. Table V), while the value is under nine in presence of an excess of sulphite (Cf. Table VII) even though the sulphite certainly contributes two to the silver equivalent and possibly more on the long runs.

A few runs were made incidentally with other developers. The data for pyrocatechol are given in Table XII and those for pyrogallol in Table XIII.

TABLE XII

Pyrocatechol 0.055g, NaOH 2.2g, variable Sodium Sulphite in 25 cc. Excess of AgBr. Temperature, ca 20°

Time	Mol Sulphite per Mol Pyrocatechol	Mol Ag reduced per Mol pyrocatechol
2 hours	0	4.4
2 hours	5	5.45
2 hours	10	5.75
3 hours	0	4.35
3 hours	5	5.5
3 hours	10	5.35
6 days	0	4.45
6 days	5	5.85
21 days	0	4.5
21 days	5	5.9

TABLE XIII

Pyrogallol 0.063g, NaOH 2.2g, variable Sodium Sulphite, in 25 cc. Excess of AgBr. Temperature, ca 20°. Time of run 1 hour.

Mol Sulphite per Mol Pyrogallol	Mol Ag reduced per Mol Pyrogallol
0	3.25
5	3.45
10	3.40

The experiments with pyrocatechol show that the reaction apparently reaches an end inside of two hours, the silver equivalent being about 4.5. When sulphite is present, there is an additional reduction of 1.0 − 1.5 mols of silver. It would probably be safe to say that about one more mol of silver is reduced in presence of sulphite. The sulphite seems to have no effect on the silver equivalent of pyrogallol. Hurter and Driffield[1] found a silver equivalent of four for pyrogallol when acting on ammoniacal silver nitrate. Andresen[2] obtained a value of two for pyrocatechol when acting on silver bromide in presence of sulphite.

The general results of this paper are as follows:

1. The silver equivalent of a developer is defined as the number of molecular weights of silver reduced from a given silver salt by one molecular weight of the developer.

2. Working with hydroquinone, Andresen obtained a silver equivalent of 2 with silver bromide and one of 4 with silver bromide in presence of sodium sulphite. Reeb obtained a value of 8 with silver oxide dissolved in sodium sulphite.

3. We have confirmed Reeb's results and we confirm Andresen's to the extent that sulphite raises the value by 2. We do not confirm Andresen's absolute figures. The discrepancy is undoubtedly due, to some extent, to lack of sufficient shaking in Andresen's experiments and may be due in part to Andresen's solutions not being sufficiently alkaline.

4. In strongly alkaline solutions and with silver bromide in excess, the silver equivalent of hydroquinone is about 6 for short runs and about 8 for long runs, at room temperature. At 100° the silver equivalent is at least 9 for short runs.

[1] Phot. Jour. *22*, 194 (1898).
[2] Namias: Chimie photographique, 264 (1902).

5. The silver equivalent for quinone is about 2 less than for hydroquinone. Quinone is unquestionably an intermediate product when hydroquinone reacts with silver bromide in absence of sodium sulphite.

6. In strongly alkaline solutions and with excess of silver bromide, the silver equivalent of hydroquinone is something over 8 in presence of sodium sulphite for short runs and about 9 for long runs.

7. The increase of 2 in the silver equivalent of hydroquinone, on short runs in presence of sodium sulphite, has been shown to be due to the fact that one mol of sodium sulphite is oxidized simultaneously with one mol of hydroquinone.

8. The apparent increase of only 1 in the silver equivalent of hydroquinone, on long runs in presence of sodium sulphite, is undoubtedly due to the formation of different oxidation products of hydroquinone in presence of sodium sulphite. This view is confirmed by the different color of the solution; but has not been tested analytically.

9. On short runs sodium sulphite increases the silver equivalent of hydroquinone by 2 if added before the run; by about 1 if added 5 minutes after the run has begun and by practically nothing if added 15 minutes before the end of a three-hour run.

10. On short runs sodium sulphite increases the silver equivalent of quinone by 1.

11. When hydroquinone reacts with silver bromide in strongly alkaline solution in presence of sodium sulphite, we have a coupled or induced reaction, one-half mol of sodium sulphite being oxidized while hydroquinone oxidizes to quinone, and one-half mol of sodium sulphite being oxidized while one mol of quinone oxidizes to something else.

12. The fact that the silver equivalents do not always come out as integers is probably not due entirely to analytical errors. We undoubtedly have the oxidation taking place along two or more different lines and we are measuring the sum of these reactions. Theoretically, there is also an effect due to concentration.

13. With ammoniacal silver nitrate the silver equivalent of

hydroquinone was nearly 7 for a five-minute run and for a two-day run. It was about 8 for an eight-day run.

14. With silver sulphite dissolved in sodium sulphite the silver equivalent of hydroquinone was about 8 for a five-minute run. No long run was made.

15. With silver oxide and caustic alkali the silver equivalent of hydroquinone was about 10.5 for a five-minute run and for a fifteen-hour run.

16. With silver bromide and with ammoniacal silver nitrate, the oxidation of hydroquinone appears to go in two stages, pretty rapidly up to a silver equivalent of over 6 and then slowly to a value of about 8.

17. With silver sulphite dissolved in sodium sulphite, the 6 stage is not detected under the conditions of the experiment, while with silver oxide a silver equivalent of 10.5 is obtained at once. It is probable that, by varying the temperature and the alkalinity, one could get a series of changes with silver oxide, perhaps beginning with 2, corresponding to the oxidation from hydroquinone to quinone.

18. Hurter and Driffield obtained a silver equivalent of 4 for pyrogallol when acting on ammoniacal silver nitrate. We get a value of a little over 3 for silver bromide on a one-hour run.

19. Andresen found a silver equivalent of 2 for pyrocatechol when acting on silver bromide in presence of sodium sulphite. We found about 4.5 for silver bromide when no sulphite was present. The discrepancy is either due to a difference in alkalinity or to experimental error in Andresen's determination.

20. In strongly alkaline solutions and with excess of silver bromide, addition of sodium sulphite increases the silver equivalent of pyrocatechol by about 1 and has apparently no effect on the silver equivalent of pyrogallol.

THE PROTECTIVE ACTION OF SULPHITE

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It is the custom to add sodium sulphite to solutions of photographic developers.[1] "The chief object of this addition is to check the rapid oxidation of the developer by the oxygen of the air. The more alkaline the developer is, the more rapidly it takes up oxygen. In consequence of this oxidation, the developer loses its strength and becomes colored more or less brown. Adding sodium sulphite to the bath decreases the oxidizing action of the atmospheric oxygen very much. Sodium sulphite belongs to the class of strong reducing agents and is oxidized by air, though very much more slowly than the organic developers. Consequently it protects a solution of a developer very effectively from the action of the air. The developer is much less readily oxidized by the oxygen of the air, when dissolved in a reducing medium such as a solution of sodium sulphite. Consequently it keeps much better."

This explanation does not explain anything. It sounds well to say that the developer does not oxidize readily when dissolved in a reducing solution; but we have oxygen present and therefore an oxidizing solution. Reiss[2] meets the difficulty more squarely though perhaps no more successfully.

"All developers are very readily oxidizable substances. If these substances were kept dissolved simply in water, they would be oxidized to some extent very rapidly by air and they would also change to some extent into hydrates which have no action on the latent image. Some substance must therefore be added to the solution of the developer which shall protect it from oxidation and shall prevent the formation of hydrates. In other words we must add something which will act as a preservative.

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[1] Namias: Chimie photographique, 269 (1902).

[2] Die Entwicklung der photographischen Bromsilbertrocken-platte und die Entwickler, 30 (1902).

The preservatives are oxidized more readily than the developers and consequently protect these latter from oxidation by atmospheric oxygen. Some of these preservatives act as restraining agents with many of the developers and retard the action of the developer on the silver sub-bromide of the latent image. Citric acid acts in this way. Other preservatives, such as the sulphites, accelerate the development. The sulphites of the alkali metals are the preservatives most commonly used; but other substances, such as tartaric acid, formic acid, acetic acid, etc., have been used with success."

Reiss commits himself definitely to the statement that the preservative is more readily oxidized than the developer and therefore protects it. The only objection to this explanation is that it does not agree with the facts. Sodium sulphite is not as powerful a reducing agent as hydroquinone, for instance, and it is difficult to see how anybody could call acetic acid a reducing agent.

Sheppard and Mees[1] are distinctly non-committal as to what really happens though they reject Reiss's explanation.

"At present the interaction of organic reducer, sulphite, alkali, and atmospheric oxygen offers some interesting problems. Sulphites have long been added to organic developers as lessening their tendency to aerial or autoxidation, and preventing the staining of the gelatine in development. This action was ascribed to a selective oxidation of the sulphite first to sulphate, the reducer being passd by. But the investigations of Bigelow,[2] S. W. Young,[3] and Titoff,[4] have shown that the oxidation of sodium sulphite in solution is greatly retarded by the presence of small quantities of substances acting as negative catalysers. Messrs. Lumière and Seyewetz have further shown that organic developers behave in this manner, so that we have here a case of an 'induced' or 'coupled' reaction[5] in which the total reaction is retarded. While the oxidation of sodium sulphite accelerates that of sodium arsenite, here are two oxidations which both proceed more slowly when the two substances are present together. It appears prob-

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[1] Investigations on the Theory of the Photographic Process, 153 (1907).
[2] Zeit. phys. Chem. *27*, 585 (1898).
[3] Jour. Am. Chem. Soc. *24*, 297 (1902).
[4] Zeit. phys. Chem. *45*, 641 (1903).
[5] J. W. Mellor: Chemical Statics and Dynamics (1904).

able that this result is due to a cycle of changes. Thus the negative catalysis with sodium sulphite has been shown to be due to the inhibition of positive catalysis (Titoff, *loc. cit.*), while the interaction of sulphite with quinone or quinonoid bodies probably accounts for the anti-oxidizing action of this, as well as its prevention of staining, since the colored bodies giving rise to this would probably be of a quinonoid structure."

Another explanation for the protective action of sulphite in the case of hydroquinone is that it regenerates the hydroquinone.[1] Mees and Sheppard[2] rather incline to this view. "When neutral sodium sulphite solution is added to quinone solution, a reaction takes place which produces a greenish-yellow color. With an excess of sulphite, this color disappears gradually. The color appears to be due to the formation of quinhydrone. The resulting solution acts as a developer. If sodium sulphite and caustic potash are added together to a quinone solution, the solution becomes colorless, the odor of quinone disappears rapidly, and the solution becomes a powerful developer. In order to study this reaction more closely, quinone was mixed with sodium sulphite which had been freed as far as possible from all sulphate. On extraction with ether, hydroquinone was obtained and identified. The aqueous solution gave no more test with barium chloride than did the blank experiment; but dithionate was present. The reaction between sulphite and quinone consists therefore in the reduction of quinone to hydroquinone and the oxidation of sulphite to dithionate."

We get a very frank confession of ignorance from von Hübl.[3] "The alkaline solutions of developers absorb oxygen from the air, become brown in color and gradually lose their developing power in consequence of oxidation. To prevent this or to reduce it to a minimum, it is now customary to add a sulphite to all organic developers. The sulphite prevents the precipitation of colored oxidation products on the silver image and therefore helps the formation of pure black negatives. It is not yet known whether the sulphite prevents the oxidation of the organic de-

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[1] Lüppo-Cramer: Wissenschaftliche Arbeiten, 20 (1902).

[2] Zeit. wiss. Photographie, *2*, 7 (1904).

[3] Die Entwicklung der photographischen Bromsilber-Gelatine-platte, 3rd Ed. 41 (1907).

veloper or whether the reaction proceeds along different lines."

If we admit that sodium sulphite does retard the oxidation of an organic developer, there are a number of possible explanations for the alleged fact.

1. The sulphite may be oxidized more readily than the developer.
2. The developer may be oxidized more readily than the sulphite; but the sulphite may regenerate the developer. This would mean that the developer acted as a catalytic agent, except for possible secondary reactions.
3. The developer may form a complex salt with the sulphite and this complex salt may be less readily oxidixed than the developer.
4. There may be no protecting action; but half the oxygen may go to the hydroquinone and half to the sulphite. In case of an insufficient supply of oxygen, this would mean an actual, though not a theoretical, decrease in the rate of oxidation of the developer.
5. We may be dealing with a case of negative catalysis.

The first explanation may be barred out because we know that sulphite is not more readily oxidized than the developer. While the experiments of Mees and Sheppard on hydroquinone support the second explanation, they were not conducting their experiments in presence of an oxidizing agent and they were working with relatively high concentration of quinone. Our experiments on the silver equivalent of hydroquinone in strongly alkaline solutions containing an excess of silver bromide give no evidence of any catalytic action of the hydroquinone and we therefore rule out the second explanation. The formation of a complex salt is quite probable because we do have an induced reaction in the case of hydroquinone and sodium sulphite. The third explanation is a possible one provided the rate of oxidation really is cut down. Since there is an induced oxidation, there would be less oxidation of the developer in presence of sodium sulphite in case one were dealing with an insufficient amount of oxygen. To this extent, the fourth explanation is correct. This would not apply in the case of pyrogallol where there is no induced reaction. The hypothesis of negative catalysis can only be possible in case there really is a decrease in the rate of oxidation in the presence of sodium sulphite. There seems to be no evidence at all on this fundamental point.

The general line of reasoning seems to have been as follows: An alkaline solution of hydroquinone, for instance, oxidizes in the air and turns brown. An alkaline solution of hydroquinone containing sodium sulphite does not turn brown in the air and therefore it has not oxidized. This neglects the possibility, definitely suggested by von Hübl, that the absence of the brown color may be due to the reaction having proceeded along different lines. Curiously enough, there was experimental evidence in regard to this, though nobody seems to have appreciated the significance of it. Sheppard and Mees[1] say that "it is of interest to note that if the solution contains a fair proportion of sulphite, and be guarded from aerial oxidation, a considerable quantity of silver may be reduced and yet the solution remain colorless. It may be concluded that in this stage no very complicated products are formed."

We have made experiments on the silver equivalent of hydroquinone in strongly alkaline solutions containing an excess of silver bromide. In a run lasting four hours and a half, the same amount of hydroquinone is oxidized whether sodium sulphite is present or not. On the other hand there is a great difference in the color of the solution, the one containing no sulphite being very much darker than the other one. A spectroscopic examination showed that the difference in color was one of intensity and not of quality. The same coloring matter is formed in the two cases; but the absolute amount is very much less in the solution containing sulphite. This difference might be due to the fact that sodium sulphite reacted with the brown coloring matter forming a nearly colorless solution or it might be due, as suggested by von Hübl, to the reaction running for the most part in another way when sodium sulphite was present. To test this, sodium sulphite was added at the end of the run instead of the beginning of the run. This did not destroy the color and therefore the cause of the solution remaining nearly colorless is that,

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[1] Investigations on the Theory of the Photographic Process, 155 (1907).

to a very large extent, we get a different reaction taking place when sulphite is present.

The general results of this paper are as follows:

1. It has been assumed that sodium sulphite protects solutions of developers from oxidation because these solutions turn brown rapidly when no sulphite is present and do not turn brown so readily when sulphite is present.
2. When solutions of hydroquinone and sodium sulphate are oxidized, they are much less brown than solutions containing no sulphite, in which the same amount of hydroquinone has been oxidized.
3. Adding sodium sulphite after the hydroquinone has been oxidized does not have the same effect on the brown color as adding it at the beginning of the run. The difference in color is therefore due to a difference in reaction products.

GLYCEROL AS SENSITIZER

BY CHARLES W. BENNETT
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Three years ago von Hübl[1] published some work on the bleach-out process. He added glycerol and found a marked increase of sensitiveness to light with methylene blue, phenosafranine, and scarlet. When a gelatine film containing 10g. gelatine and 3 cc. glycerol was stained with methylene blue, the color bleached completely in an hour's exposure to sunlight. With a film containing no glycerol, no change was observed in the same time. From his experiments von Hübl concludes that the light-sensitiveness of methylene blue is increased five hundred to a thousand-fold by the addition of glycerol. No explanation is offered for this rather remarkable result.

Wurster[2] states that it is a well-known fact that glycerol makes oxygen active; but he gives no reference and we have not yet been able to find any authority for this statement. This is not of any great importance, however, because further consideration made it seem probable that the bleaching was not due to oxidation. Methylene blue can bleach by reduction or by oxidation. When the bleaching is done by reduction, the color comes back when the reduced dye is exposed to air. Now von Hübl found that the blue color reappeared when the prints were kept in the dark. This made it seem probable that sunlight caused glycerol to react with oxygen forming glyceric aldehyde, especially as it had already been noticed[3] in Manila that sunlight converts methyl alcohol to some extent into formaldehyde.

To test this point various concentrations of glycerol were placed in glass flasks and were exposed to a powerful arc lamp. Distinct evidence of the presence of an aldehyde was obtained by means of the fuchsine test. Glycerol, which had been acted on by light,

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[1] Phot. Mittheilungen, *46*, 253 (1909).
[2] Ber. chem. Ges. Berlin, *19*, 3211 (1886)
[3] Freer: Philippine Jour. Sci. *5* B, 8 (1910).

was found to bleach methylene blue, safranine, and Biebrich scarlet appreciably at 50° in the dark. In presence of sunlight the dye would react more rapidly. It was also shown that solutions of acetaldehyde bleach these three dyes in the dark, although slowly.

It was also found by von Hübl that an addition of arsenates and glycerol increased the sensitiveness of methylene blue. Since arsenates as such could only increase the light-sensitiveness of methylene blue by acting as an oxidizing agent, it is clear that there is an error of some sort here. Since no details are given, it is impossible to say whether von Hübl really used sodium arsenite instead of arsenate, or whether the reaction takes place faster in two stages, the aldehyde from the glycerol reducing the arsenate to arsenite and the arsenite reducing the methylene blue. Whichever explanation one adopts, the arsenite is the important substance theoretically. It is interesting to note that Limmer[1] found a sensitizing effect due to what he calls arsenic trioxide, in the absence of glycerol. It seems probable that he was using sodium arsenite though he does not say so.

The general results of this paper are:

1. When glycerol and air are exposed to a bright light, an aldehyde is formed, presumably glyceric aldehyde.
2. Methylene blue, safranine, and Biebrich scarlet are bleached in the dark by acetaldehyde or by a solution of glycerol which has been exposed to light, the reaction taking place faster at higher temperatures.
3. The sensitizing action of glycerol on certain dyes, as discovered by von Hübl, is due to the formation of the aldehyde.
4. Dyes, which are not bleached by reduction, will not be sensitized in this way.
5. The alleged sensitizing action of arsenates in presence of glycerol is really due to arsenites.

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[1] Zeit, angew. Chem. *1909,* 1715.

PHOTOCHEMICAL REDUCTION OF COPPER SULPHATE

By Charles W. Bennett
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Since light tends to eliminate from a solution, the ions by which it is absorbed, it follows that light tends to deposit copper from a solution of copper sulphate. The reverse tendency, however, is so great that no visible effect is obtained even in the strongest light. Reducing agents, likewise, tend to separate metallic copper from the sulphate solution. If, however, the potential of the reducing agent be low enough, the effect is merely a tendency, without actual reduction, as in the case of light. Light, therefore, in the case cited above, acts as a mild reducing agent.

In order to show the reducing action of light on copper sulphate solution, it ought to be possible to obtain a reducing agent so mild that the copper would not be reduced in the dark, but would be reduced by the combined action of light and the mild chemical reducing agent. In other words, the effect would be additive, the final reducing power being the algebraic sum of the two tendencies.

Several reducing agents were studied in an attempt to obtain a suitable one. Hydrazine sulphate with copper sulphate gives an insoluble blue compound which renders its use objectionable. Hydroxylamine hydrochloride also deposits an insoluble compound. The decomposition products of pyrogallol, as well as those of hydroquinone in alkaline solution, hindered satisfactory work with these reagents. If copper sulphate or acetate be made ammoniacal and enough hydrazine hydrate be added with the exclusion of air, the blue of the solution is discharged, and metallic copper is deposited as a mirror on the walls of the containing vessel, with the simultaneous separation of cuprous oxide. The strength of the reducing agent may be varied by varying the quantity of the hydrazine hydrate solution used.

To show the effect of light on the above named combination, twelve test tubes were fitted with corks through which pin holes had been made, and 10 cc. of a 1 per cent solution of copper acetate, with 10 per cent of concentrated ammonium hydroxide was placed in each tube. To the two sets of six tubes each, were added respectively, 3.5, 4, 4.5, 5, 5.5, and 6 cc. of an 0.5 per cent solution of hydrazine hydrate. After being corked, one set was placed in the dark while the other was exposed to the light from a 2.5 kw Macbeth carbon arc printing lamp, for seven hours. The temperature was 17° C. in both cases, cold water being used to cool the tubes exposed to the arc. The first two tubes showed no reduction in either light or dark. The remainder of the tubes in the light deposited a reddish brown precipitate which dissolved upon shaking the mixture up with air. The product was probably largely cuprous oxide with a small amount of pulverulent copper, the reducing action being too mild to give the copper mirror. The product obtained in the dark in the corresponding four tubes was quite different in both quality and quantity. A very small amount of a muddy blue deposit, resembling a basic copper salt, was obtained.

On account of the fact that this solution is colorless, and that there is a simultaneous deposition of cuprous oxide, showing that the copper must be formed by the reduction of the intermediate cuprous ion, it seemed advisable to seek a stronger reducing agent which would reduce the copper sulphate solution to metallic copper, directly from the blue solution. A blue solution was desirable for the effective light seemed to be the visible rays, since glass containers were used.

The use of phosphorus was suggested at once. R. Böttger[1] noticed that phosphorus when heated with copper sulphate solution gave metallic copper which then reacted with more phosphorus to give copper phosphide. It was also noticed that the reduction went on very readily in direct sunlight, when powdered phosphorus was allowed to act on the solution absorbed

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[1] Jahresbericht ü. d. Fortschritte d. Chem. u. verwandter Theile anderer Wissenschaften, *1857*, 107.
Jour. prakt. Chem., *70*, 430 (1857).
Pogg. Ann. *101*, 453 (1857).
See also Senderens: Comptes. rendus. *104*, 177 (1887).

by paper or cloth fiber. The substance becomes heated to about 35° C. and the rise in temperature was presumably taken for the cause of the reduction. Mrs. Fulhame[1] found, previous to this, that an ether solution of phosphorus reduced copper sulphate solution readily. This use of an ether solution offers the possibility of varying the reducing power, by changing the phosphorus concentration of the solution. It was, therefore, decided to place ether solutions of phosphorus of varying concentrations over copper sulphate solution, and expose in the dark and in the light. To prevent change of concentration, as well as to exclude air, the ether solution was added under the lip of an inverted crucible which was filled with a copper sulphate solution and stood in a crystallizing dish holding the solution. The ether solution displaced the copper solution from the inverted crucible, floating to the top where volatilization was prevented and air was excluded. In order to be able to use ultra-violet light, transparent quartz crucibles were used. A mercury lamp could then be suspended over the crucibles.

A 5 per cent solution of $CuSO_4\ 5H_2O$ was used. The ether solutions were made by diluting, presumably, a saturated solution of phosphorus in ether. Pieces of the element were allowed to stand in ether with intermittent shaking, for several days. This solution was diluted and used, with the attempt to get the concentration such that reduction would occur in the light but not in the dark. The carbon arc referred to above was finally used, the results obtained being caused by visible light, most likely.

Results of two parallel experiments showing the point at issue, are given. One cc. of the saturated phosphorus solution was diluted with ether to 10, and another to 20 cc. Portions of these solutions, about 5 cc. each, were placed over two sets of copper sulphate solution, one set being placed in the dark and the other exposed to the light from the arc.

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[1] An Essay on Combustion, London, 60 (1794).
Mellor: Jour. Phys. Chem. 7, 562 (1903).

The temperature was 19.5° C. The results are tabulated below.

5 per cent copper sulphate solution. 19.5° C.
Solution 30″ from arc

20 cc. of ether solution contained cc's of saturated solution	In light	In dark
2	Phosphide after 2 hours	Phosphide after 6 hours
1	Phosphide after 6 hours	No phosphide obtained

The last solution, therefore, was not strong enough to reduce the copper when acting alone, but by the aid of the reducing action of the light, combined with its own tendency, the reduction was accomplished.

In conclusion, it may be stated that,

1. Light reduces ammoniacal copper solutions in the presence of weak reducing agents, like a dilute solution of hydrazine hydrate.
2. Light reduces copper sulphate solution in the presence of a dilute ether solution of phosphorus.
3. Light tends to increase the reducing power of reducing agents, thereby making possible reductions which would not take place in the dark.

EXPERIMENTS ON CRYSTALLOLUMINESCENCE

By E. F. Farnau
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That cathodoluminescence is due to chemical reaction was first suggested by Wiedemann and Schmidt[1]. This assumption was later confirmed by Wilkinson[2], who showed that the same quality of light was emitted on excitation of the salts by cathode rays, as in their formation from their decomposition products. The decomposition products refer to those produced by cathodo-excitation, and are in some cases actually visible in the residue after exposure to the emanation.

It was of interest to determine the quality of crystalloluminescence of some of the salts to see if it corresponded with that of cathodoluminescence and chemiluminescence.

Bandrowski[3] observed that light was emitted on precipitation of alkaline halides by alcohol or concentrated hydrochloric acid, but has given only brief description of the color. His experiments were repeated in order to note more carefully the quality of crystalloluminescence.

After half an hour's wait in the dark-room until the eyes became sufficiently sensitive, 50 cc. of each of the salts, sodium and potassium chloride, bromide, and iodide were shaken with 50 cc. of alcohol in a 100 cc. graduate and the glow appearing during precipitation was observed. In similar manner concentrated hydrochloric acid was employed as precipitant of the chlorides of sodium and potassium. The results as tabulated indicate the identity in quality of the luminescence whether produced by cathode rays, chemical combination, or precipitation.

[1] Wied. Ann., *54*, 622 (1895); *56*, 203 (1895); *64*, 78 (1898).
[2] Jour. Phys. chem., *13*, 691 (1909).
[3] Zeit. phys. chem., *15*, 323 (1894); *17*, 234 (1895).

COLOR OF LUMINESCENCE

Salt	Cathode	Reaction	Precipitation
NaCl	bluish white	blue	bluish white
NaBr	bluish white	blue white	bluish white
NaI	greenish white	white	greenish white
KCl	bluish white	blue	bluish white
KBr	blue	blue	blue
KI	green	greenish white	green

SUMMARY

The same quality of light is emitted in chemical reaction, as cathodoluminescence, and as crystalloluminescence in the case of the halides of sodium and potassium.

This research was suggested by Professor Bancroft, and has been carried out under his supervision. It is a pleasure to acknowledge my indebtedness for his kindly interest.

Abstract

THE EFFECT OF PRESSURE ON THE COLOR OF AMORPHOUS SUBSTANCES

BY E. F. FARNAU
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It was noted by Tafel[1] that long exposure of zinc oxide to canal rays caused darkening of the compound without appreciable loss in its weight. He ascribed the discoloration to the bombardment by the particles and substantiated this view by submitting zinc oxide in a screw-press to a pressure of about 50,000 atmospheres, and by grinding the oxide in a mortar whereby extremely high local pressures are obtained;— in each of these cases, darkening of the zinc oxide occurred. A pressure of 500 atmospheres in a hydraulic press caused no color change.

Furthermore, while the colorless oxide showed strong green anodoluminescence, none of the discolored varieties were active, nor was the oxide when prepared by precipitation of zinc sulphate with sodium carbonate, washing, and ignition at the temperature of the Bunsen burner. Tafel writes: "We must thus distinguish at least three forms of zinc oxide—a yellow-brown and two white. The colored and one of the white forms possess the property of fluorescing unred action of canal rays." As a classification this is admirable; but unfortunately no explanation is offered,—first, for the color change of the compressed oxide, unless tossing it into the scrap-heap of illdefined allotropic modifications constitutes an explanation; and, second, for the loss of ability to fluoresce under anodo-excitation.

It is true that in the latter instance, Schmidt's[2] explanation that zinc oxide shows anodoluminescence only when impurities are present, is rejected by Tafel on the grounds that the zinc oxide prepared by precipitation with sodium carbonate, which

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[1] Drude's Ann., *11*, 613 (1903).
[2] Drude's Ann., *9*, 707 (1902).

surely contains adsorbed sodium salt, did not show fluorescence. This would seem to be a step backward, for it is well known that while traces of impurities increase the luminescence of many salts, larger amounts either produce no further effect or actually cause a decrease until the luminescence has quite disappeared. Doubtless the preparation of zinc oxide by precipitation with sodium carbonate belongs to this latter class in that it contains too much impurity, and had the zinc been precipitated with ammonium carbonate instead, a much purer product would have been obtained which would have shown anodoluminescence.

A very simple and direct explanation of the color change of the oxide under pressure can be given. Amorphous zinc oxide, i.e., the supercooled liquid, when massive may be assumed to be yellowish, but in finely divided condition, as obtained for example by combustion of zinc or ignition of one of the salts, is colorless. The same thing is observed on powdering copper sulphate or potassium dichromate or discolored rock-salt, each becoming lighter as the degree of fineness increases, until finally the substances are practically pure white. The explanation in terms of optics is obvious.

On the other hand, grinding may produce quite the opposite result; e.g., if on the one hand arsenic or antimony be rubbed in a mortar, the crystals are broken up and a state of greater subdivision obtains; but if lead or gold powder be similarly treated, the particles do not become finer, but are merely spread out, i.e., burnished, and where they overlap are welded together, giving in each case the characteristic metallic lustre. In like manner, zinc oxide will show this effect of burnishing, save that here the substance, being transparent, will give the color of its transmitted light. The phenomenon is not restricted to zinc oxide but is shown equally well by many amorphous substances, bismuth oxide, stannic oxide, zinc sulphide. Waentig[1] observed it in the case of phosphorescent alkaline-earth sulphides.

The decrease in fluorescence of dissolved substances is of common observation. It is probably due to absorption of the active emanation by the discoloring impurity. If in the case of zinc oxide the discoloration under anodic excitation is solely due to a

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[1] Zeit. phys. Chem., *44*, 499 (1903).

mere pressure effect, and no decomposition occurs, it could be accounted for by decrease of the total surface of the substance, since the effect of anodic and cathodic excitation is only superficial.

In order to imitate in the case of zinc oxide the *crushing* effect of grinding, the brittleness of the oxide was increased by pouring liquid air upon it in a porcelain mortar. If it be ground under the liquid air no discoloration is observed. On the other hand some, discolored by grinding at ordinary temperature, was ground under liquid air;—it became colorless.

A simple illustration of both the crushing and burnishing effects of grinding is afforded by a judicious manipulation of the confection known as horehound candy. This usually comes as "drops" of a dull brownish-yellow color, and is doubtless amorphous. If the material be subjected to sharp taps of the pestle it can be broken up into particles somewhat smaller than grains of granulated sugar, and as such is considerably lighter in color than the original candy. If now the mass is rubbed slowly and with considerable pressure on the pestle, the particles reunite and a brown smear of the candy is left sticking to the mortar.

These observations shed light on another set of phenomena,—the change of color of oxides when hot and cold. Zinc oxide when heated in a matrass in the Bunsen flame becomes yellow, but returns to its original color when cold. Bismuth oxide and stannic oxide, similarly treated, become darker when hot and lighten in color when brought back to room temperature, but do not become white again. Any one who has seen potter's glazes will recall their sad whitish hues. These glazes are prepared by pouring the brilliantly colored melted glaze into water, whereby the material is broken up into fine particles each in a state of strain such that grinding increases still further the degree of fineness. After painting on the ware, proper heat treatment causes agglomeration of the particles and the brilliant color is restored. The color-changes of oxides hot and cold are doubtless due at least in part to the same thing. Cooling of the heated oxides causes disintegration of the coalesced particles, and in their original fine state of subdivision the masses show more or less their original color. This disintegration is not complete in the case of bismuth and stannic oxides.

An experiment was carried out of heating the surface of zinc oxide contained in a crucible with the point of an oxy-hydrogen flame. A good deal of volatilization of the material occurred, but on cooling, whereas the mass of material regained its original color, that which had sintered together by immediate contact with the flame remained yellow on cooling. It is still yellow after several months. The analogy is evident between the results of this experiment and the making of a poor and a good joint in glass-blowing.

SUMMARY

The color of amorphous zinc oxide in mass is yellow. This accounts for its darkening when compressed and when heated.

It is a pleasure to express my appreciation of Professor Bancroft's kindly advice and criticism during the progress of this research which was undertaken at his suggestion.

THE EFFECT OF TEMPERATURE ON CATHODOLUMINESCENCE

By E. F. Farnau

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Carefully purified and dried cadmium sulphate when exposed to cathode rays shows little or no luminescence[1], neither fluorescence, phosphorescence, or thermoluminescence; and no visible decomposition occurs after excitation. If a trace of sodium, potassium, lithium, or zinc sulphate is present, it glows with a brilliant yellow color under excitation, and shows visible decomposition into brown cadmium oxide. Sulphur trioxide is doubtless the other reaction product.

On the other hand, the reaction of cadmium oxide with sulphur trioxide causes a similar yellow chemiluminescence, which leads one to account for the cathodoluminescence by the assumption that under the cathode rays decomposition of the salt occurs with formation of cadmium oxide and sulphur trioxide, which in turn recombine to yield the original salt, the recombination causing emission of light. This hypothesis is further borne out by the fact that in whatever manner the luminescence of cadmium sulphate is produced, whether by cathode rays, the ultra-violet light of the iron arc, as thermoluminescence, or as chemiluminescence in the reaction of cadmium oxide with sulphur trioxide,—the quality of light is the same, namely, yellow.

Since the light is caused by a chemical reaction, its intensity will vary with the conditions affecting the rate of the reaction, e.g., temperature and catalytic agents. The effect of the impurities referred to above is doubtless due to their action as catalytics in hastening the reaction. It was suggested by Professor Bancroft that an experiment be devised to show the change of luminescence with temperature.

The cathode tube used consisted of two parts, into the upper of which was sealed the disc cathode and ring anode, the lower part holding the salt. A two-cylinder Geryk oil-pump maintained

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[1] Wilkinson, Jour. Phys. Chem., *13*, 719 (1909).

the vacuum. The extremely pure salt was exposed in the tube to the cathode emanation and showed little or no luminescence at ordinary temperature. It was hoped that raising the temperature of the substance would produce cathodoluminescence. But here a difficulty arose—either due to slow expulsion of occluded gases in the salt or of adsorbed moisture in the glass, or to increased permeability of the glass to air at the higher temperature, the vacuum dropped off, as indicated by the decrease in the characteristic green fluorescence of the glass in the cold parts of the tube. This naturally precluded any possibility of success of the experiment.

It was decided, since rise in temperature produced such disastrous effects, that the reverse could be tried. The purified salt was replaced by a well-dried commercial sample, which under cathodo-excitation glowed brilliantly at ordinary temperature. All of the tube save about ¼ in. of the bottom was wrapped with cotton gauze and jacketed in glass. Liquid air was poured on the gauze until it was saturated. The vacuum improved considerably as evidenced by the increased cathodoluminescence of both the salt and the glass of the tube. When the vacuum was at its best, the salt, still at room temperature, was cooled by immersion of the bottom of the tube in liquid air. As the salt cooled its luminescence decreased, as did that of the glass until it finally became barely visible. The experiment was repeated a number of times, the salt being brought alternately to room temperature and to that of liquid air—the luminescence correspondingly increased and diminished.

The experiment was repeated with potassium bromide, which ordinarily shows a bright blue cathodoluminescence, with like results.

SUMMARY

1. From the assumption that all forms of luminescence are due to chemical reaction, the deduction can be drawn that those conditions increasing the rate of chemical reaction will increase the intensity of the luminescence.

2. Experiments on the effect of temperature on the luminescence of cadmium sulphate and potassium bromide yield results

in accord with the hypothesis; the salts although luminescent at ordinary temperature lose almost all of their activity at the temperature of liquid air.

I wish to acknowledge my indebtedness to Professor Bancroft who suggested this research, for his generous advice, criticism, and encouragement.

COLOR-PHOTOGRAPHY OF LUMINESCENCE

By E. F. Farnau and J. M. Lohr
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The colors of luminescence from various sources are generally difficult to describe. When one considers the variation in description of ordinary colors, brilliant and well illuminated,—differences due to personal whim in definition, or to color-blindness, or even to carelessness in observation,—it is not a matter of surprise that the color of luminescence, often very faint, should be a matter of dispute. Obviously the correct solution of the difficulty is by the use of the spectrograph; but here another disadvantage obtrudes. The luminescence at best is in most cases very faint, and being further diminished by use of a slit (a cylindrical lens could be used to advantage) and absorption and reflection by the lenses and prisms of the apparatus, to say nothing of the ultimate dispersion of the light, necessitates tiresomely long exposures. Probably for this reason most of the investigation of phosphorescence[1] has been restricted to that of the brilliantly luminescent uranium salts and the impure alkaline-earth sulphides.

During an investigation of several kinds of luminescence, Professor Bancroft suggested a partial remedy. This consisted of actual photography in colors of the light. This has been done, and the present paper deals with the preliminary results of the experiments.

The Dufay Color-plates employed consist of glass plates covered with parallel rulings of green and violet-blue inks and rulings of red ink set vertical to these;—the whole being covered with a panchromatized sensitive film. A ray filter gives correct rendition of colors. These plates are claimed to be much faster than the Lumière Autochrome.

The first use made of the color-plates has been in reproducing the colors of luminescence by cathode rays. Cathodoluminescence was excited by exposing substances contained in an 8 in. by $1\frac{1}{2}$ in. cathode tube consisting of two halves connected by a ground

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[1] Nichols and Merritt, and their students, Phys. Rev., passim.

joint, the lower half containing the substance, the upper half the ring anode and disc cathode. A two-cylinder Geryk oil-pump was used to maintain the vacuum. A good-sized induction coil furnished electrical energy. The disastrous effects of X-rays, so easily avoided in the prism spectrograph, were prevented by the simple device of screening all of the tube with lead foil save a small window just above the substance under excitation, and by means of a mirror directing the visible light upon the plate placed in a position not exposed to the X-rays.

In these preliminary experiments, photographs were taken of the light from highly luminescent minerals such as willemite (yellow-green) and fluorite (deep blue), and from a red-fluorescent sulphide.

The results are encouragingly successful,—exposures of even five minutes giving plates in which the color is easily distinguishable as that of the fluorescence. Investigation by this photographic method of the quality of light emitted during the much fainter cathodoluminescence of the salts of the alkaline halides is now in progress.

SUMMARY

Successful use is made of color-photography to determine the quality of the visible light emitted during cathodoluminescence.

Abstract

WHY NOT TEACH PHOTOGRAPHY?

By Francis C. Frary
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Nowadays few of the workers in photography understand the theory of the processes they use. This makes their experimental work largely empirical, and throws all the burden of progress upon the manufacturer and a very few workers. The manufacturer can hardly be expected to devote much energy to building up new processes so long as the market for his goods is as good as it is at present.

Scientific investigation of photographic chemistry is needed, and we must train chemists in the processes of the present so that they may know where improvement is needed. The importance of photographic training for scientists other than chemists is urged, and the fact that other sciences are depending more and more upon photography in their progress is pointed out. The author pleads for the teaching of photography or photochemistry in the colleges of the country, as a branch of chemistry which is worthy of the attention of the student.

THE DIRECT PRODUCTION OF POSITIVES IN THE CAMERA BY MEANS OF THIOUREA AND ITS COMPOUNDS

BY FRANCIS C. FRARY, RALPH W. MITCHELL AND RUSSELL E. BAKER
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The increasing use of transparent positives in photographic processes inspired us to begin the study of methods for their direct production in the camera. It was hoped that such a process could be developed as would make it possible to produce lantern-slides, transparencies, and positives for use in the Askau process, without first making negatives. It was also hoped that the process would enable us to shorten the manipulation in the Lumière Autochrome and similar processes in color-photography. This work was begun nearly two years ago by Messrs. Frary and Baker, and was continued during the past year by Messrs. Frary and Mitchell.

Waterhouse[1] first described the use of thiourea in the direct production of positives, and recommended the use of the double salt, tetra-thiourea-ammonium bromide. His work seems to have attracted little attention, however, and apparently the results obtained with thiourea by others[2] were unsatisfactory. Recently Perley[3] has worked on this method, apparently obtaining more satisfactory results, using a hydrochinon developer instead of the eikonogen developer recommended by Waterhouse. But his directions are not very explicit, all his work was done on lantern-slide plates, which are quite different from ordinary plates, and we found that attempts to make positives according to his directions were seldom successful, and then only to a limited extent.

Working according to his directions, and using ordinary plates, we found it very hard to get results at all concordant, when all

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[1] Eder: Jahrbuch für Photographie, *16*, 170 (1892).

[2] Nipher: Trans. Acad. Sci. St. Louis, *10*, 210 (1900). Quoted in Jour. Phys. Chem. *13*, 237 (1909).

[3] Jour. Phys. Chem. *13*, 649 (1909).

the conditions appeared to be the same. Using thiourea as he recommended we obtained fair positives, fogged plates, and hybrids, all under the same conditions of exposure, strength of developer, and time of development. It appeared that there was another factor capable of exercising a great influence, and this was found to be the temperature of the developer.

We have made about 600 plates in all by this process, and find that the predominant factors in the control of the results are: (1) brand of plate, (2) proportion of thiourea or its salts, (3) developing agent, (4) proportion of alkali, (5) proportion of restrainer, (6) character of thiourea salt used, (7) temperature of developer, (8) method of applying the thiourea compound. For uniformity, most of our plates have been made by printing under a lantern-slide at a distance of 1½ meters from a standard candle, the apparatus being set up in the dark room, and the candle thoroughly protected from draughts of air.

We find that the developer which gives the best results depends quite largely on the brand of plate used. This is not wholly a matter of the relative speed of the different plates, but seems to depend on the composition of the emulsion. Best results are obtained with plates of only moderate speed, such as the Cramer Banner X or the Seed 26. Most of our work has been done on the Cramer Banner X plate; after working out the effect of variations of the conditions on this plate, other plates were used for comparison. We have used Seed 26, 27, 30, process, and lantern-slide plates, Vulcan plates, Lumière Blue Label, and Lumière Sigma plates. In some cases the developer had to be modified to get the best results.

When the thiourea was used as a separate bath before development, as recommended by Perley, it was used in a 1:1000 solution. When mixed with the developer, the same strength was used, in proportions varying from 30 to 40 parts per 100 parts of developer. Equal parts of the two solutions seem to give the best result; less thirourea has too great a tendency to give hybrids, and more produces excessive fog.

We find that different developing agents have different effects. The hydrochinon formula recommended by Perley [Sol. A: water, 100, sodium sulphite (dry) 12.6, hydrochinon 2.1 gm.; Sol. B:

water 100, sodium carbonate (dry) 25.2 gm.] was the one which seemed to work best, and was used in most of the experiments. Satisfactory positives were also obtained with an adurol developer containing a rather large amount of alkali, but dianol and amidol were unsatisfactory. The effect of metol is very peculiar. A small amount of it added to the regular hydrochinon developer increases very much the density of the negative image which develops first, but acts as restrainer for the positive image. Hybrids generally result, although by decreasing the exposure very much and developing for a very short time, some rather poor positives could be obtained.

In general, the more alkaline the developer, the stronger the positive and the weaker the negative image obtained. The effect of the thiourea compounds seems to be dependent very largely on the presence of a large amount of alkali. With some plates (Seed Process, Lumière Blue Label, and Vulcan) the amount of carbonate in the developer above-mentioned, which was excellent for the Cramer Banner X, must be considerably increased to get the best results. With Seed Lantern Slide Plates, the best results were obtained by reducing the sulphite and diluting the developer. With adurol the amount of carbonate required was four times that recommended by the manufacturers for development of the negative, or more than that required for the regular hydrochinon developer. Less than the proper amount of carbonate in any developer produces hybrids; more produces brown fog. The color of the resulting image is also dependent on the amount of carbonate in the developer, as well as the amount of sulphite, the developing agent, temperature, time of development, and brand of plate.

One strange thing about the process is the relatively large amounts of potassium bromide that are required to produce any restraining effect on the developer. It requires cubic centimeters where one would use drops in the ordinary development. As much as 7 cc. of a 10% solution has been used in 100 cc. of the mixed developer (1 part A, 1 part B, 2 parts thiourea solution), the only effect apparent being increased time required for development. If thiourea be used the addition of some bromide is advantageous, and the same is true of tetra-thiourea-ammonium bromide. But tetra-thiourea-ammonium chloride seems to work better without any restrainer, Acetone sulphite was a vigorous restrainer, but seemed to hold back the half-tones more than the shadows, tending to give harsh results. Potassium iodide was a very much more powerful restrainer than the bromide; the latter being easier to control was generally used when a restrainer was necessary.

The tetra-thiourea-ammonium bromide, recommended by Waterhouse, but apparently not tried by Perley or other investigators, was very much superior to the simple thiourea, giving clearer and better positives. Most of the work was done with it. The corresponding chloride salt, however, appears to be better still, and works without a restrainer. The iodide was not very satisfactory. All these salts were prepared according to the directions of Reynolds.[1] We would prefer the chloride, as far as our experience goes, although the bromide is a great improvement on the plain thiourea.

One of the most important factors in the process is the temperature of the developer, and this appears never to have been noticed by any one. Control of all the other factors failed to give us reproducible results until the temperature was considered. For the method recommended by Perley (bathing in thiourea solution, with subsequent development) the best results were obtained at about 24°, much lower temperatures (18 to 20° C.) giving hybrids, while higher temperatures (28 to 29°) gave very strong positives, with a heavy brown fog. This fog was troublesome at all times with this separate-bath process, unless the temperature was so low that the negative image came up so strongly as to make the result a hybrid. In the use of the thiourea or its compounds in the developer, as we prefer, the temperature may vary from 12 to 20° C., but temperatures of 15 to 18° C. (60 to 65° F.) seem to give the best results. Higher temperatures result in rapid development, with production of fog; low temperatures decrease the speed of development, and especially the development of the positive. At temperatures as low as 7°C. the negative image could be developed, but no positive image was obtained below about 11°. This effect of temperature seems to be independent of the effect of all the other variables.

[1] Jour. Chem. Soc. *59*, 384, (1891).

As indicated above, we find that we obtain much better results by mixing the solution of the thiourea compound with the developer, in the proportion of 1:1 than by using it as a separate bath. In the latter case more trouble is found with fog, the results are more irregular, and tend to be spotted, the time of development and the difficulty of control are increased. Using the two solutions together, the development is much the same as the ordinary process, except that it takes less time.

The following procedure is recommended for the development of positives on the Cramer Banner X plate. The exposure is made in the ordinary way, and should be a little longer than for the production of a negative. Double the normal exposure will usually be about right. The hydrochinon developer recommended on a previous page is used, mixing one part of A, one part of B, and two parts of a 1:1000 solution of either thiourea, tetra-thiourea-ammonium bromide or tetra-thiourea-ammonium chloride, preferably the latter. If thiourea is used, 0.5 cc. of 10% potassium bromide are added per 100 cc. developer; if the ammonium bromide compound be used, 2 cc. of the bromide solution per 100 cc. developer; while if the ammonium-chloride compound is used no restrainer is needed.

Develop as usual, keeping temperature of developer between 15 and 18° C., the negative image first appears, then the plate appears to fog, and soon the positive image can be seen by transmitted light. Care must be taken not to over-develop, as the positive image will be quite strong. Rinse, fix, and wash as usual. If the negative image is too strong, it indicates over-exposure; the plate may be reduced slightly with the Farmer reducer. A foggy positive, with practically no negative, indicates under-exposure, if the temperature of the developer has been kept within the proper limits. Development is rapid, being usually complete within four minutes. The positive image is characterized by its color; with the above conditions it will be red, warm sepia, or purplish red. The negative image is black and very transparent.

For making lantern-slides, the exposure will in general be less than that required to make a negative under the same conditions, and the developer should be diluted with an equal volume of water. If, however, the subject to be reproduced be a line-drawing, full strength developer and normal exposure may be used, followed by slight reduction. This will give excellent contrast. In fact the principal fault of the process from the viewpoint of the slide-maker is the large amount of contrast obtained; the range from high-light to shadow is as great as in a good negative, consequently the slides of scenes tend to be too heavy in the shadows. This defect is minimized if an ordinary plate is used instead of a lantern-slide plate.

Excellent positives have been obtained on films from an Eastman Film-pack. They were made with the regular developer, using the tetra-thiourea-ammonium chloride. The gradation and density thus obtained were excellent, and the films would make good lantern-slides.

For Cramer Crown, Seed 26 and 27 plates the procedure recommended for the Cramer Banner X plate is satisfactory. For Seed process plates, 4 gm. anhydrous sodium carbonate should be added to each 150 cc. of the normal developer above recommended, and for Lumière Blue Label Plates, 6 gm. carbonate per 150 cc. developer. The latter brand of plate did not give us very satisfactory positives under any circumstances; we are inclined to believe that the lot which we used had been kept too long before we obtained them.

The process works well with the Lumière Autochrome plate, using the normal developer diluted with an equal amount of water, but the strong red color of the image spoils the color rendering, so until this color can be modified the process does not seem to be applicable to this plate. In the earlier part of our work, rather remarkable results were obtained with these plates, by bathing them for one minute in 1:1000 thiourea solution before developing, and using the regular metaquinone developer and reversing solution recommended by the manufacturers. Results obtained indicated that good plates could be obtained with about $\frac{1}{6}$ of the exposure otherwise necessary. These plates were made in the laboratory, the strength of the light being controlled by observations with the Watkins Bee Meter. However, recent attempts to duplicate these results on short exposures out of doors have been unsuccessful.

SUMMARY AND CONCLUSIONS

The conditions for successfully carrying out the Waterhouse process of producing positives have been carefully studied, and are given in detail. The most important of these is the temperature of the developer.

The double salts formed by thiourea with ammonium bromide and chloride work better than the thiourea itself. The amount of restrainer used varies with the salt used.

The character of the developing agent and the quantity of alkali in the developer play an important part in the process; a strongly alkaline hydrochinon developer is recommended, and the thiourea solution should be mixed with this as needed for use.

The process gives positives of excellent detail, with about the gradation and density of a first-class negative. The exposure is relatively short, being about double that required for the production of a normal negative.

THE MICRO-STRUCTURE OF WET-PLATE NEGATIVES

By Francis C. Frary and Guy H. Woolett
University of Minnesota, Minneapolis, Minn.

Little work has been done upon the micro-structure of the physically developed photographic image. Bellach[1] has studied the effect of variation of conditions upon the grain of negatives made in the ordinary way upon dry plates, and incidentally made a few measurements of the grain upon dry plates where the image had been developed from 17 to 48 hours by a physical developer. No one seems to have studied the grain of the wet-plate, where the development is purely physical, but extremely rapid, lasting less than a minute.

The original object of the work here described was to study the effect of the various operations of development and intensification upon the grain of the wet-plate. But no definite grain could be obtained either on the undeveloped plate or on that which had been developed and fixed but not intensified. After the first intensification[2] the grain became clearly visible; six subsequent intensifications did not change its size, as we had supposed they would, but only increased the capacity of the grains of silver. The grain was rather fine for measurement, so attempts were made to change the developer in such a way as to produce coarser grains which could be examined more easily.

The developer which we had used was the one regularly employed in this laboratory for all wet-plate work, consisting of a solution of ferrous sulphate testing 20 on the hydrometer (Argentometer), to which 60 cc. of acetic acid per liter had been added. The collodion used contained 1.3 gm. cotton, 0.67 gm. cadmium iodide, 0.44 gm. ammonium iodide and 0.07 gm. calcium chloride per 100 cc. and was that which we regularly used in wet-plate work.

The use of a weak acid pyro developer did not give the desired results, so the ferrous sulphate developer was modified by diluting

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[1] Die Struktur der photographischen Negative, Halle a/S, 1903.

[2] By immersing in cupric bromide, washing, and immersing in silver nitrate.

with an equal volume of water. This reduced the speed of development, and we supposed that the size of the grain would be increased. Actually the opposite result was obtained, as will be seen by comparison of the photomicrograph of a plate thus developed (Fig. 1) with that of one developed with the regular developer (Fig. 2). In using this diluted developer, it was found that the exposure had to be doubled in order to produce a normal negative. The average diameter of the grain with normal developer appeared to be 0.002 to 0.003 mm.

From the above we reasoned that increasing the strength of the developer should increase the size of the grain and decrease the exposure required. Experiment showed that this was the case: using a developer of double strength (ferrous sulphate testing 40, with acetic acid 180 cc. per liter) the time of exposure was halved, and the diameter increased (Fig. 3) to from 0.005 to 0.009 mm.

Upon again doubling the strength of the developer (sulphate testing 80, to which 420 cc. acetic acid per liter were added) the exposure was still further decreased and the grain enlarged (Fig. 4).

The exposure required at F/11 when using the regular developer was 1½ minutes, doubling the strength of the developer produced normal negatives in ¾ minutes, while doubling the strength again gave good negatives in 15 seconds. As this last developer was practically saturated with respect to ferrous sulphate, no attempt was made to increase the concentration beyond this point.

It was noticed that in such strong solutions the ferrous sulphate appeared to reduce the acetic acid to acetaldehyde, the odor of which was always present in old developer. Increase of acidity seemed to reduce this tendency somewhat.

Another plate was given a normal exposure, and then after washing out all the silver nitrate from the film it was developed with the regular developer, to which 10 drops of 10% silver nitrate per 100 cc. had been added. This gave a mixed grain, as shown in Fig. 5.

In all these plates there is seen a background of smaller grains which appear to be alike and uniform under all conditions. They appear to be of the same size as the grain obtained with the regular developer (Fig. 2) and may probably be considered to be the normal

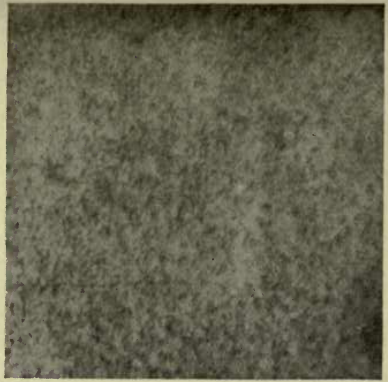
Figure 1.

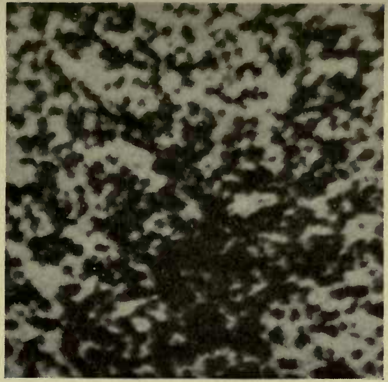
Figure 2.

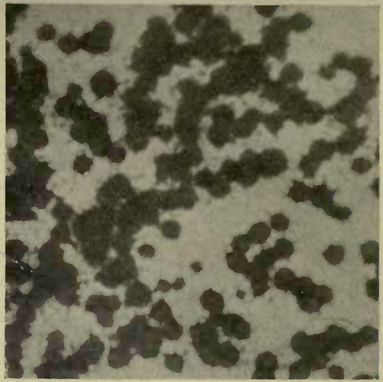
Figure 3.

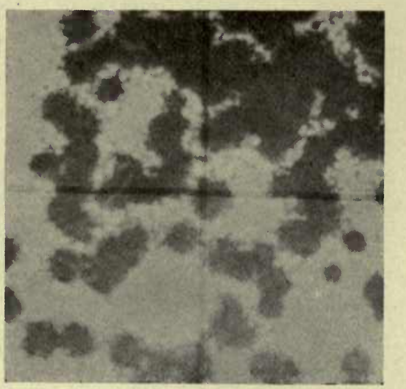
Figure 4.

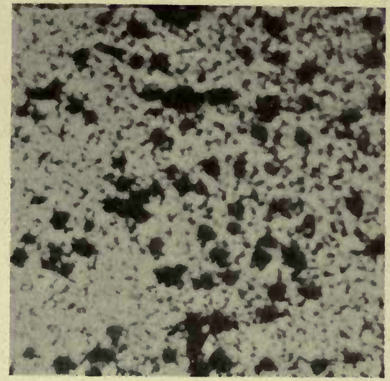
Figure 5.

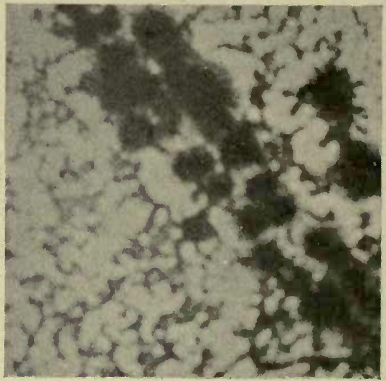
Figure 6.

grain of the image. The larger particles seem to be formed by the knitting together of a group of smaller ones as indicated by the fact that the latter often form a sort of fringe around the former. In Fig. 6 this structure appears at a maximum. This is a photomicrograph of a part of an "oyster shell" marking found on a plate developed with some of the double strength developer to which an insufficient quantity of acetic acid had been added. As this "oyster shell" had no foundation in the latent image, it would be inferred that the particles started as very small grains which grew to their present size by combining with one another.

To see whether the larger grains came from silver halide formed by one of the salts present, and the smaller grains from the rest, a series of collodions was prepared containing each of the salts alone. Passable negatives were obtained with the collodions containing only cadmium or ammonium iodide, but that obtained with the calcium chloride was very poor. In all cases, however, the grain obtained followed the same rules as in the normal emulsion.

Inquiry among photoengravers has shown that the possibility of reducing the exposure by increasing the strength of the developer has been known to a few of them, but so far as I can find, it is not at all generally known, and it is not mentioned in any textbook which I have seen.

SUMMARY AND CONCLUSIONS

The size of the predominant grain in the wet-plate negative depends wholly on the concentrations of the ferrous sulphate and the silver nitrate in the developer.

By increasing the strength of the developer normal negatives may be obtained with as little as $\frac{1}{6}$ of the normal exposure.

Intensification with cupric bromide and silver nitrate does not change the size of the grain appreciably, but increases its opacity.

The large grains obtained with strong developers appear to be made of aggregations of smaller ones.

SUNLIGHT

By Paul C. Freer[1] and H. D. Gibbs
Manila, P. I.

Five years ago, the study of the effect of tropical sunlight was commenced in this laboratory by the investigation of certain chemical reactions which are catalyzed by light. The causes of the coloration of phenol and aniline were first studied and the reaction products isolated. Since prior attempts in this direction in other parts of the world had proved to be a failure, we naturally surmised that the reactions were more rapid in the Tropics, producing products in sufficient quantities to facilitate their identification, a conclusion which, at this time, we do not feel was entirely justified. By means of a chemical photometer, comparisons of light intensities in various localities, in and out of the Tropics, showed that on clear days the rates of reaction were practically uniform in all of the places investigated. The work was then extended to the study of the effects of the sun's rays upon experimental animals and upon human beings. A statement of the results obtained in all of these phases of the work is given in this paper.

The influence of sunlight in the Tropics has been the subject of extended discussion for many years and the intensity of insolation has generally been considered to be the dominating factor. In considering the question of what may be regarded as a tropical climate, we are too apt to be influenced by preconceived opinions, and to lose sight of the fact that there is as much difference between tropical climates as between those in the temperate zone. It can readily be understood that a place recognized to be within the Tropics, may, by reason of its proximity to the sea, its altitude,

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[1] Paul C. Freer, M.D., Ph.D., director of the Bureau of Science, Manila, P. I., died on April 17, 1912. This article is written by H. D. Gibbs, chief of the Division of Organic Chemistry, Bureau of Science, and associate professor of Chemistry, University of the Philippines, Manila, P. I. It was our intention to contribute several articles to the Eighth International Congress of Applied Chemistry, on the sunlight work carried on in the Philippine Islands. The entire work is summarized as briefly as possible in this one paper.

its relation to mountain chains and other natural surroundings, have a climate so modified that the actual sunlight may have less influence than in localities which are situated upon the borders of, or even well within, the temperate zones.

The races native to the Tropics, where the absence of a pronounced winter is favorable to the rich development of microscopical life, have no knowledge of bacteriology and pathology which would enable them to understand protective measures to avoid infectious and other diseases, and as a rule they do not have access to the complete food supplies of persons in temperate zones. As a consequence, many of the ill effects which are attributed to sunlight, may, in reality, be due to entirely different causes. The subject under discussion is so complex and is influenced by so many factors that, at the present time, general conclusions, excepting in so far as they are borne out by experimental evidence, are premature.

A STUDY OF CERTAIN CHEMICAL REACTIONS CATALYZED BY SUNLIGHT

It long has been known that some benzene derivatives, such as most phenols and amino compounds, undergo changes in the light with the formation of colored compounds. In the case of phenols, one of us has shown that the formation of the colored compounds is due to oxidation which, in every case examined, results in the production of quinones. While decompositions and condensations set in, the first and most important colored compound formed is a quinone. In the sunlight, the reactions involved depend only upon the presence of oxygen, and the mechanism of the reactions can be explained by the presence of the labile hydrogen atom. The activity of the various phenols can be predicted by the presence of enol-keto tautomers, which Baly[1] and his co-workers have shown can be determined from the study of the absorption spectra of the compounds in solution. This tautomeric condition is recognized through the formation of an absorption band which lies in the ultra-violet region of the spectrum. When the enol-keto

[1] Baly and Collie: *Jour. Chem. Soc.*, London *87*, 1339 (1905); Baly and Eubank: *Ibid.*, *1348;* Baly and Desh: *Astrophys Jour.*, *23*, 118 (1906); Baly and Marsden: *Jour. Chem. Soc.*, London (1908) *93*, 2108 (1908).

tautomers are in the pure state, this band disappears, and its presence is characteristic of the coexistence of the tautomers in dynamic equilibrium. The tautomeric process occurring in acetyl acetone and analogous aliphatic compounds causes a band similar to that produced by aromatic compounds, and in the same region of the spectrum.

The fixation of the labile hydrogen atom, precluding the formation of enol-keto tautomers, and in some cases the fixation of the hydrogen atom para to the hydroxyl group cause changes in the behavior of the absorption band and chemically increase the stability of the molecule. Aniline and methyl aniline give absorption spectra which indicate the existence of the labile hydrogen atom.

In the presence of moisture and oxygen, the sunlight oxidation may be attributed to hydrogen peroxide, for this oxidizing agent is formed by the action of sunlight upon water and oxygen[1] and it has been found that in the dark, hydrogen peroxide and other oxidizing agents will produce the same result as those obtained in the sunlight. In the consideration of a structure of the benzene ring, the behavior in the sunlight of this class of compounds, containing the so-called labile hydrogen atom, is very suggestive.

It is possible that the reactions hereafter described do sometimes proceed at a more rapid rate in Manila than in higher latitudes; even if this is true, no reliable evidence is thus introduced that the sunlight is more active in the Tropics, for the temperature of the solutions exposed to the sunlight often rises to approximately 50°, and all of these reactions have high temperature coefficients.

Phenol[2]. — This compound colors very rapidly in the sunlight in presence of oxygen. The principal compound formed is quinone and the presence of the brilliant red condensation product, phenoquinone, is highly probable. The crystals do not color so long as moisture and liquid phenol are absent and, it seems, that the crystals are the enol form, while the liquid contains both enol and keto tautomers. Anisole undergoes no change in the sunlight.

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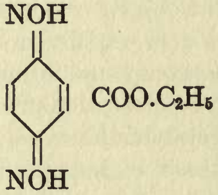
[1] Gibbs: The question of the production of hydrogen peroxide by the action of sunlight on water and oxygen. *Phil. Jour. Sci., Sec. A. 7*, No. 2 (1912).

[2] Gibbs: The compounds which cause the red color in phenol. *Phil. Journ. Sci., Sec. A. 3*, 357 (1908), and The oxidation of phenol; The effect of some forms of light and of active oxygen upon phenol and anisole, *Ibid.* 4, 133 (1909).

The cresols. — The three cresols all color in the sunlight, the meta most rapidly and the ortho and para compounds much more slowly. The methyl ether of para cresol remains colorless.

The hydroxy benzoic acids and their esters. — The meta compounds color most rapidly, the ortho next, and the para not at all. The esters color more rapidly than the free acids. The presence of oxygen is necessary and the cause of the coloration is oxidation. The oxidation of the meta and ortho hydroxy benzoic acids should produce the same compound as that formed from gentisic acid, namely, the para quinone of benzoic acid. This compound has been studied, and, while it has not been isolated in sufficient quantities for purification and analysis, there is every indication that it does not of necessity break down, giving off carbon dioxide as has been stated.[1]

Quinol carboxylic acid (Gentisic acid). — The esters of this acid color more rapidly in the presence of oxygen and sunlight than any of the other compounds studied. The free acid is also rapidly affected. The oxidation of the ester is easily affected in the cold by hydrogen peroxide, very dilute solutions of potassium dichromate, and potassium persulphate acidified with dilute sulphuric acid and other oxidizing agents. Potassium persulphate with dilute sulphuric acid seems to produce the best results although it is very difficult, in all cases, to carry the reaction to completion without, at the same time, causing decomposition. No evidence of decomposition to para quinone has been detected in the cold.

The oxime  described by Jeanrenaud[2] has not been prepared but the monooxime $C_6H_3:O,:NOH,.COO.C_2H_5$ has been prepared by D. C. Pratt, by the oxidation of the ester

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[1] Nef: *Ber.* Chem. Ges. Berlin, *18,* 3499 (1885).

[2] *Ber.* Chem. Ges. Berlin, *22,* 1783 (1889).

with hydrogen peroxide in the presence of hydroxylamine-hydrochloride.[1]

Aniline.[2]— Pure aniline colors very rapidly in the sunlight. In presence of oxygen, the colored compounds, azobenzene, 2, 5-dianilinoquinone, dianilinequinoneanil, and azophenine have been isolated. All of these are soluble in aniline, producing red solutions. In the absence of oxygen, *i.e.*, in the presence of indifferent gases such as hydrogen and nitrogen, or invacuo, the coloration is also very rapid and the principal products are azophenine, benzene, and ammonia.

Methylaniline and dimethylaniline. — Methyl aniline also colors rapidly in the sunlight and methylamine has been identified as one of the reaction products. Dimethylaniline colors much more slowly. Since no especial methods were employed to purify this compound, it is possible that the slight coloration observed after sixty days' exposure may be due to impurities.

Methyl alcohol. — Ciamician and Silber[3] have found that ethyl alcohol and quinone react in the sunlight forming acetaldehyde and quinol. Methyl alcohol[4] and quinone produce formaldehyde and quinol. Methyl alcohol in presence of oxygen and sunlight or hydrogen peroxide in the dark is oxidized to formaldehyde.

COMPARISON OF SUNLIGHT INTENSITIES

The actual number of hours of insolation per year on the earth's surface, where the sky is always clear, is greatest at the equator and diminishes toward the poles, the ratio between latitudes 0° and 45° being 1.83 to 1.34, although in the longer days in the temperate zone the sunshine reaching the earth when the sun is near sunrise or sunset is only a small proportion of that at midday. In the Tropics we have greater absorption and radiation by the earth's surface, factors which naturally vary with different regions

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[1] Gibbs, Williams, and Pratt: *Phil. Journ. Sci.*, *Sec. A.* *7*, No. 2 (1912).

[2] Gibbs: The compounds which cause the red coloration of aniline: I. The effect of oxygen and ozone and the influence of light in the presence of oxygen; II. The effect of sunlight in the absence of oxygen, etc., *Ibid.* (1910), *5*, 9, and 419.

[3] *Gazz. Chim.* (1886) *16*, 111 (1886); and *Ber. Chem. Ges.* Berlin, *34*, 1532 (1901).

[4] Gibbs: The action of sunlight upon methyl alcohol. *Phil. Journ. Sci.*, *Sec. A.*, *7*, No. 2 (1912).

according to the hours and intensity of insolation and the color of the surface exposed, being least with the green surfaces of vegetation[1].

In the higher latitudes, the hours of insolation during the short days are so few and during the night the hours of radiation so many, that the surface of the earth steadily cools at certain times of the year, making one of the factors which causes a winter season.

Many instruments have been devised to measure the sunlight intensity and, while many are useful, all fall short of accomplishing the desired result. The involved regions of the spectrum are too extensive and are subject to too great relative variations to permit of grouping as a whole for purposes of comparison.

The Angström pyrheliometer which records the total normal insolation in heat units is probably the most successful device for a general comparison, but, in the ultra-violet, its sensitiveness is much inferior to other means of measurement which we have at hand.

The chemical photometers fail for the reason that they are only sensitive to their characteristic restricted regions of the spectrum, and their usefulness is limited to comparisons of these regions. For the ultra-violet and adjacent portions of the visible spectrum, the uranyl acetate-oxalic acid solution is the most satisfactory, although it is open to several objections which will be pointed out later.

I. THE ANGSTROM PYRHELIOMETER

This instrument is the best devised for comparisons of total insolation and is most sensitive to the longer wave lengths. Such data as are available have been gathered by Dr. Herbert H. Kimball of the Mount Wilson Observatory[2]. Comparisons are made of the annual maximum intensity of solar radiation at various points as follows:

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[1] Hann: Handbuch der Klimatologie, *2*, 23 (1910), calls attention to the measurements at Chinchochro, Laoango coast, near the equator. The regular measurements of the surface of the earth exposed to the sun gave temperatures over 75°, often 80°, and at one time nearly 85° C.

[2] *Bull. U. S. Mt. Wilson Obs.*, *3*, 100 (1910).

Station and latitude	Intensity
Cape Horn, 55° 31′ S.	1.47
Washington, 38° 54′ N.	1.44
Montpelier, 43° 36′ N.	1.60
Modena, 44° 39′ N.	1.37
Kief, 50° 24′ N.	1.39
Warsaw, 52° 13′ N.	1.35
Hald, 56° 25′ N.	1.32
Katherinenburg, 56° 50′ N.	1.58
Pavlovsk, 59° 41′ N.	1.48
Upsala, 59° 51′ N.	1.35
St. Petersburg, 59° 56′ N.	1.47
Treurenburg, 79° 55′ N.	1.29

These variations are not great, and, such as appear, are attributed by Kimball to instrumental, rather than to atmospheric conditions. Angström[1] records comparisons of Guimar (altitude 360 meters) and Alta Vista (altitude 3,352 meters) in Teneriffe (20° 30′ north) as 1.38 for Guimar and 1.618 for Alta Vista, the latter high figure to be expected from the altitude.

The maximum observed by Dr. Rudolph Schneider at Vienna (48° 13′ north)[2] was 1.524 in February, and figures ranging from 1.00 to 1.455 are quite frequent; indeed, the observations for the time near the noon hour in Vienna, although averaging somewhat lower, bear a remarkable resemblance to those in Washington, when we consider that Kimball worked only on clear days and Schneider made observations on days of partial cloud and even of fog. Mr. Harvey N. Davis, working at Providence, Rhode Island, in ten months observed a maximum of 1.328 occurring in March, and, in general, his figures also bear a striking resemblance to those obtained in Vienna. Kimball, in discussing the annual march of radiation as compiled by him, stated that "a rather surprising uniformity throughout the year [is shown] in the maximum intensity of radiation, the December minimum being only 8 per cent less than the April maximum." The departure by months from the average quinquennial mean shows that there is a

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[1] *Astrophys. Jour., 9,* 342 (1899).

[2] *Jahrb. d. k. k. Zentralanstalt f. meteorol. w. Geodyn., N. F. 43,* 12 (1906).

considerable variation by years, amounting to a minus quantity of as much as 18 per cent on the average for the year 1903. This diminution was widespread and such low times are periodic; the same is probably true of high periods, so that the absolute amount of insolation on the earth's surface may vary from year to year,[1] but frequent enough or of great enough intensity to alter the picture as a whole.

Although the maximum radiation at the various points mentioned is very similar in all, yet, if we take the annual totals, we find differences for such points as have been compared. Kimball[2] has calculated the average monthly totals for Washington and Warsaw for normal surface, and from them we can obtain the yearly totals, which for Washington are 254,026 and for Warsaw 216,200, so that Warsaw actually has 85 per cent of the radiation received at Washington, although it is 14° farther north. Unfortunately, pyrheliometer readings for places in the Tropics are not at hand. We ordered an Angström pyrheliometer nearly a year ago, but the instrument has not yet arrived. When it does, we will begin readings in Manila and thus obtain comparative data.

II. THE CHEMICAL PHOTOMETER, THE URANYL ACETATE-OXALIC ACID SOLUTION

The most effective means yet discovered for comparing the intensities in the ultra-violet and adjacent regions of the visible spectrum are obtained from the rate of decomposition of the uranyl acetate-oxalic acid solution,[3] which has been utilized extensively in the laboratory of organic chemistry, Bureau of Science, first by Bacon,[4] whose preliminary paper on the subject has formed the basis for later work. The absorption spectrum of this solution is under investigation and this study will be published

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[1] Kimball: *Ibid.*, *114*, 115.

[2] *Ibid.*, 103.

[3] The solution finally adopted in this laboratory consists of five cubic centimeters of a one-per-cent solution of uranyl acetate, 5 cubic centimeters of a 10-per-cent oxalic acid solution (hydrated), and 20 cubic centimeters of water.

[4] *Phil. Journ. Sci.*, *Sec. A.*, *2*, 127 (1907); *5*, 281 (1910).

later. The other factors which influence the rate of reaction are the nature of the background, the size, shape, and material of the flasks in which the solution is exposed, and a small temperature coefficient.[1] While the reaction is complicated by more factors of importance than was originally believed and is by no means a perfect indicator, there is no doubt that, when the solution is properly employed, it affords a very useful means for comparison of light intensities of the region in which it is sensitive. Having determined the basis of the investigation, colleagues in various parts of the world were asked to coöperate by a series of measurements with calibrated flasks and standard solutions exposed to the sunlight between the hours of 9 and 12 on a dull black surface, removed from side reflections. Returns from Manila (latitude 14° 36′ north) (Table I); Baguio (latitude 16° 25′ north) (Table II), Philippine Islands; Honolulu,[2] Hawaii Territory (latitude 21° 18′ north) (Table III); Kuala Lumpur,[3] Federated Malay States (latitude 3° 10′ north) (Table IV); Khartoum,[4] Egypt (latitude 15° 36′ north) (Table V) in the Tropics; and Washington,[5] D. C. (latitude 38° 59′ north) (Table VI); Tucson,[6] Arizona (latitude 32° 12′ north) (Table VII); and Munich,[7] Germany (latitude 48° 8′ north) (Table VIII) are now available, and are given in the following eight tables.

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[1] Bruner and Kozak: *Zeit. f. Elektro chemie*, *17*, 354 (1911), state that the reaction has no temperature coefficient but with this we do not agree. The question is, at present, under investigation.

[2] Through the kindness of the Hawaiian Agricultural Experiment Station, Dr. E. V. Wilcox, in charge, Mr. W. T. McGeorge making the titrations, using a 200-cubic-centimeter Erlenmeyer flask which has been sent to this laboratory for standardization.

[3] Through the kindness of the Institute for Medical Research, Dr. Henry M. Fraser, director, Mr. M. Barrowcliff making the titrations; a quartz flask was used.

[4] Through the kindness of the Wellcome Research Laboratories, Dr. Andrew Balfour, director, Dr. W. Beam, chemist.

[5] Through the kindness of Dr. Raymond F. Bacon, Bureau of Chemistry.

[6] Through the Kindness of Dr. H. Spoehr, Desert Laboratory.

[7] Through the Kindness of Professor Doctor Wilhelm Muthmann, Königlich Bayer. Technische Hochschule.

TABLE I. — *Manila*

Month	Average	Maximum	Minimum	Mean maximum	Mean minimum	Average temperature	Observatory thermometer readings	Black bulb readings	Clear days
1910									
May	13.21	17.7	3.21	15.42	6.88	32.09	37.2	46.9	10 out of 27
June	12.62	17.1	6.08	15.87	10.05	32.85	38.0	47.6	8 out of 25
July	13.74	17.8	4.61	15.95	10.07	33.37	36.6	47.6	7 out of 24
August	13.11	17.5	5.11	15.14	10.07	31.27	39.3	49.3	3 out of 25
September	10.94	17.1	1.15	13.51	6.05	30.30	35.2	47.2	4 out of 26
October	11.78	17.45	1.71	13.88	9.33	30.61	35.5	45.9	4 out of 26
November	9.97	17.38	1.47	13.78	6.16	28.57	33.8	44.5	1 out of 24
December	10.03	14.61	1.19	12.44	7.12	29.18	33.1	43.9	3 out of 22
1911									
January	12.69	17.64	7.99	14.91	11.20	30.51	35.1	45.3	5 out of 19
February	11.54	16.32	4.98	14.01	7.97	30.14	34.0	42.0	5 out of 22
March	13.13	17.35	4.64	15.24	10.45	......	36.6	46.0	11 out of 25
April	13.88	17.60	10.49	15.94	12.41	......	37.4	48.0	6 out of 17
May	13.27	15.09	10.28	15.48	13.06	......	39.1	50.3	11 out of 22
June	14.07	16.38	12.80	15.00	13.42	......	37.9	49.5	6 out of 17
July	11.83	14.06	7.11	13.18	10.22	......	35.7	45.1	0 out of 11
Average	12.45	16.82	5.52	14.65	9.64	30.889	36.3	46.6	

TABLE II. — *Baguio*

Months	Average	Maximum	Minimum	Mean maximum	Mean minimum	Observatory thermometer readings	Black bulb readings	Clear days
1911								
March	12.5	18.7	6.9	16.2	8.2	....	....	5 out of 13
April	16.1	20.6	8.3	17.9	12.1	27.3	51.2	3 out of 19
May	16.2	19.4	11.1	17.7	14.0	27.5	51.4	
June	11.9	16.7	7.1	.....	.....	....	....	
Average	14.2	18.8	8.3	17.1	11.4	....	....	

TABLE III. — *Honolulu*

Months	Average	Maximum	Minimum	Mean maximum	Mean minimum	Average temperature	Clear days
1911							
January	11.78	17.40	3.77	14.67	7.47	21.1	0
February	13.49	16.71	6.29	15.57	10.72	21.1	7 out of 21
March	13.82	17.76	3.48	16.26	9.48	21.6	15 out of 25
April	14.30	17.99	5.46	16.04	10.83	22.8	13 out of 24
May	13.85	17.64	7.89	15.87	10.62	21.1	9 out of 26
June	13.64	17.41	6.62	15.46	11.34	21.1	15 out of 25
July	12.45	16.85	5.53	14.53	9.35	21.1	3 out of 25
August	14.58	18.51	9.08	16.28	11.92	21.6	10 out of 23
September	15.30	20.77	6.57	17.07	12.02	21.1	12 out of 20
October	14.96	18.37	8.24	16.46	12.47	21.1	14 out of 24
November	15.0	18.62	6.23	16.48	12.63	23.5	11 out of 23
December	12.7	17.0	6.7	15.87	9.76	22.5	11 out of 23
1912							
January	14.45	16.13	13.56	15.31	13.86	22.5	4 out of 5
Average	13.9	17.8	8.9	15.8	10.9	21.7	

TABLE IV. — *Kuala Lumpur*

Months	Average	Maximum	Minimum	Mean maximum	Mean minimum	Clear days	Temperature
1911							
March	15.27	17.3	12.2	16.70	13.56	5 out of 11	31.57
April	15.21	17.5	10.4	16.76	12.79	10 out of 18	32.56
May	15.25	17.5	9.0	16.66	11.25	7 out of 23	32.42
June	15.45	17.3	12.2	16.7	13.97	5 out of 13	32.80
July	14.53	17.3	9.3	15.6	13.09	5 out of 26	32.72
August	15.39	18.1	11.6	16.2	13.62	6 out of 25	32.06
September	15.94	17.5	12.0	16.91	13.99	11 out of 21	31.76
Average	15.29	17.5	11.0	16.52	13.18		32.27

TABLE V. — *Khartoum, Egypt*

Months	Average	Maximum	Minimum	Mean maximum	Mean minimum	Maximum temperature	Clear days
1911							
September	17.4	19.6	14.8	17.8	16.5	40.2	12 out of 22
October	17.8	20.8	16.1	18.7	17.3	38.9	22 out of 31
November	18.2	19.2	15.4	18.9	17.3	39.7	24 out of 30
Average	17.8	19.5	15.4	18.5	17.0	39.6	

TABLE VI. — *Washington, D. C.*

Months	Average	Maximum	Minimum	Mean maximum	Mean minimum	Clear days
1910						
June	9.91	12.70	6.54	11.55	7.18	5 out of 8
July	11.19	15.60	1.70	12.80	7.19	10 out of 14
August	10.37	15.75	1.85	12.75	6.81	8 out of 10
September	11.38	19.14	3.83	13.49	8.37	10 out of 18
October	12.91	16.66	4.37	15.05	10.16	14 out of 16
November	11.29	17.33	3.54	14.38	8.82	4 out of 9
December	11.51	15.85	5.00	14.15	9.27	8 out of 11
1911						
January	12.97	16.42	9.52	14.77	11.53	8 out of 9
February	15.01	20.34	9.66	20.07	11.64	4 out of 5
March	11.96	12.63	11.29	12.63	11.29	3 out of 3
April	13.09	13.48	12.32	13.48	12.32	
Average	11.96	15.99	6.33	14.10	9.50	

TABLE VII. — *Tucson, Arizona*

Date	Average	Maximum	Minimum	Mean maximum	Mean minimum	Clear days	Average temperature
1910 October	11.5	13.4	7.7	.....	.....	4 out of 6	28.7
1911 December	14.44	18.47	6.07	16.21	11.15	15 out of 20	19.8

TABLE VIII. — *Munich*

Date	Average	Maximum	Minimum	Mean maximum	Mean minimum	Clear days	Average temperature
June	13.10	16.89	5.25	15.55	9.65	4 out of 12	18.5
July	14.72	17.49	6.76	16.16	11.68	14 out of 31	22.9
August	13.91	18.15	4.80	16.31	8.91	13 out of 31	22.3
September	10.29	17.05	0.81	13.97	5.47	8 out of 30	17.2
October	7.54	14.41	1.35	10.37	3.61	3 out of 31	10.0
November	3.42	9.71	0.56	6.48	1.55	0 out of 30	5.1
December	2.39	6.09	0.36	3.86	1.30	0 out of 21	1.3
January	1.74	3.75	0.64	3.13	0.81	0 out of 5	2.4
Average	8.39	12.94	2.56	10.73	5.37		11.8

The figures are all given in per cent of oxalic acid decomposed in one hour and are, so nearly as possible, reduced to uniform conditions.

In Manila (Table I) the average per cent of oxalic acid decomposed for one hour during one year was 12.45, with a maximum of 17.8 for the highest observed day, and a minimum of 1.15. The average of all days above the general mean was 14.65 and below, 9.64. Strange to relate, the lower average in Manila did not fall during the rainy months of July to October, but occurred in November, and the clear months of January, February, and March did not show so high a figure as the comparatively cloudy ones of June and July.

Kuala Lumpur (Table IV) shows a slightly higher average, 15.29 as against 12.45, and a somewhat higher maximum (18.1 against 17.8) and a much higher minimum, namely, 9.0 as against 1.15 for Manila. On average clear days in Kuala Lumpur the insolation in regard to the rays under discussion is practically the same as in Manila, but the cloudy and hazy weather of our island climate shuts off a proportion of the sunlight. The total effect is that of a climate having less insolation, and the difference between two places, one practically on the equator and the other 14° north, is a meteorological one, and not due to any excess *per se* of the shorter wave lengths in the former locality.

Honolulu (Table III) shows an average of 13.9 or 1.45 higher than Manila and only 1.39 lower than Kuala Lumpur. It had an abnormal maximum in September, 1911, of 20.77, or higher than either of these tropical places, and a minimum of 3.48. However, the average of days above the average mean is 15.8 as against 16.52 for Kuala Lumpur. No months in Honolulu are so low as the lowest in Manila (September, December; 10.94 and 10.03 respectively). Therefore, Honolulu (21° 18′ north) has, as regards the photocatalytic action of the sun's rays, a condition much like that of Manila (14° 36′ north) and Kuala Lumpur (3° 10′ north), and the extraordinarily high days observed at that place indicate that, at times, the atmosphere on Hawaii is so free from disturbances, strata of varying density, or haze, as to allow even a greater proportion of the rays having photocatalytic action to reach the surface of the earth than is the case in the localities nearer the equator. No one will venture to state that the sunlight is more oppressive in Honolulu than in the Philippines; indeed, the general temperature is lower, the average temperature at the time of the observation was 21°.1 to 22°.6, where ours in Manila was 30° to 25°. The difference among these three places under discussion is so slight that we can say that practically the photocatalytic action in all is the same.

Unfortunately, only a few data have reached us from Tucson, Arizona (32° 12′ north) (Table VII), and these for the months of October, 1910, and December, 1911. They show a maximum of 18.47, or 0.67 higher than that of Manila, and a minimum on one day of 6.07. The temperature during the observation averaged about as it does here (28°.7), and higher than at Honolulu. Doubtless, when a longer series of observations from this interesting point is at hand, we shall discover many days in Tucson where the maximum is as high as, or higher than, in Manila, and an average about the same.

The data from Washington need a little more careful analysis, as the methods followed were not always identical with the ones adopted by us as a standard, and the hours of insolation were not always the same. The results, recalculated to conform so nearly as possible to our conditions, are recorded in Table VI. So far as they are comparable, the results show that Washington, which has a winter season, presumably more atmospheric disturbances, many cloudy days, and possibly but few absolutely clear days, can show at times as much effect as the four places discussed and an astonishingly high average of 11.96. One day in September gave the hourly decomposition, between 8.45 and 12.15 in the morning, of 19.14 per cent. Making allowance for the greater concentration of uranyl acetate used by Bacon, the totals in Washington are lower by about 33 per cent than in Manila, excepting the one month, November, in Manila with an average of 9.97.

The results in Khartoum, Sudan (Table V), are extremely interesting and, perhaps, the most instructive of the series. Khartoum is close to the desert and in about the same latitude as Manila. We find here, in observations extending through the months of September, October, and November, an average of 17.8 as measured by a standard quartz flask, or as much as 5.35 higher than Manila and 2.5 higher than Kuala Lumpur, but this average is so high because of the remarkably uniform character of the insolation, the minimum being 14.8 as against 9.0 for Kuala Lumpur and 1.15 for Manila. The maximum observed day at Khartoum was 20.8, which is higher than any observation at Manila by 3.0 and 2.7 more than the highest observed at Kuala Lumpur, only two other observed days approaching this, one of 20.8 at Honolulu and the other 20.6 at Baguio in the Philippines, at an altitude of 1,445 meters. In Khartoum, out of sixty-six days of observation, no less than fifty-two gave decompositions between 16.7 and 17.9, and eleven between 17.9 and 18.6. In Khartoum, therefore, we have a remarkably uniform, high insolation so far as the portion of the spectrum under consideration is concerned: but, nevertheless, the days of maximum illumination do not materially differ from those in the other localities, so that the absolute intensity of the ultra-violet illumination which may reach the earth on perfectly clear days is practically the same, the only distinctions being meteorological. If we consider this uniformly high rate and its causes, it is evident that the reverse can also be true and it would be possible to have so-called tropical climates where cloud interference and other causes would bring the average illumination below that in temperate zones. The temperatures of observations at Khartoum were somewhat higher than at Manila and Kuala

Lumpur, but we observe that days of maximum temperature are not necessarily days of maximum photocatalytic decomposition.

The conditions at Munich (latitude 48° 8′ north) are, in a measure, directly opposed to those at Khartoum. Here, during November and December, there were no clear days and the average decomposition for these months was 3.42 and 2.39 per cent respectively. On clear days, during the months of June, July, August, and September, the maximum decomposition very closely approached the maxima obtained in other places.

Another interesting comparison is furnished by Bruner and Kozak[1] working in Krakau (53° 40′ north) on bright, sunshiny days in the spring and summer, the solutions in test tubes being exposed between the hours of 10 and 2. The background is not stated; but, as they worked before an open window, it is to be presumed that reflections did not play so important a part as with flasks placed on white paper, although the buildings had to be considered. Since the work was done in test tubes, we can not accurately compare results. Owing to the shape of the container, the variation might be considerable in amount, nevertheless, these authors, with a solution corresponding to our standard, obtained a decomposition of 15 as the maximum in their observations, so that it is apparent that, even in this latitude, days occur with a photocatalytic reactivity sufficiently high to be comparable with those in the Tropics.

In order to compare a climate at higher altitude and but little north of Manila with that of the latter city itself a series of observations was made at Baguio (Table II) (altitude 1,445 meters). The temperatures of the nights and in the shade of Baguio are so low that it is, in many respects, an ideal resort for recuperation from the lowland climate, yet the photocatalytic action is much the same, except that the maximum at Baguio is higher than in the lowlands (20.6 as against 17.8), being in this respect like Honolulu (20.7). The average is 14.2, or 1.75 more than in Manila and 1.09 less than Kuala Lumpur and 0.30 more than Honolulu. The black-bulb readings are practically the same. At Baguio, as is to be expected, we encounter a climate in which the rays undergoing investigation are somewhat more intense than in the lowland. The

[1] *Loc. cit.*, *35.*

average temperature in the sun during the observations was 7° to 8° lower than in Manila.

Manila and Baguio, at present, are the only places where the black-bulb thermometer readings are available simultaneously with the photocatalytic measurements, and a study of individual days demonstrates that the two figures, namely, black-bulb readings and percentage of oxalic acid decomposed, are not by any means functions of each other; indeed, within reasonable limits they seem to be independent. Of course, it is understood that a certain relationship exists, because, naturally on clear, bright days both black-bulb and photocatalytic readings will be high, and both the reverse on cloudy ones. As an example of these variations, we can cite a few figures taken from daily observations:

TABLE IX.—*Comparison between photocatalytic and black bulb readings in Manila*

From 9 to 12 a.m.	Weather	Photocatalysis	Black bulb (mean of 3 observations)
1910			°C
April 28	Clear	15.4	52.0
May 7	Clear	17.7	52.5
May 16	Slightly cloudy	13.4	54.0
May 18	Clear	16.4	52.0
June 9	Clear	14.7	54.5
July 5	Slightly cloudy	16.6	56.3

Comparisons of this kind can be extended almost indefinitely, but those given suffice to show that, in the same place and on apparently equally clear days, the relative proportions of the rays in the various portions of the sun's spectrum may vary considerably.

The supposedly injurious effect of tropical sunlight has been attributed, in a large measure, in the greater part of the literature, to the action of the more refrangible rays of the sun's spectrum, lying in the region of the violet and beyond in the ultra-violet, and to them have been attributed even grave morphologic changes sufficient to bring about permanent differences in races of the human family. So far as this work has gone it seems to develop that, if the so-called "actinic" rays in Manila are particularly objectionable, they are the same in Honolulu and, for a certain time of the year, even in Washington and other places. However, the more we consider the ultra-violet rays of the sun's spectrum, taking cognizance of the fact that nowhere, whether in or out of the Tropics, do they extend beyond 291[1] μμ, understanding what a large proportion, if not all, of the direct rays are subjected to molecular scattering, reflection, absorption, and dispersion by the upper layers of the atmosphere, and, noting the slight differences between the lowlands at Manila and highlands at Baguio, we are forced to the conclusion that, on clear days, when the sun is at the same angle, they are everywhere much alike in intensity. Indeed, it appears as if the greater part of these rays which reach the earth are diffused and not direct. In concluding this topic, we must observe that it may be possible that we receive rays the nature of which we have not yet determined and which, with our present physical technique, we are not likely to determine and which may have an influence in the phenomena of insolation. The discovery of such rays, if they exist, will form an interesting and important part of this subject.

THE EFFECT OF SUNLIGHT UPON ANIMALS

The air temperatures at higher altitudes are lower than in the lowlands although the effect of sunlight upon animals and solid objects, such as the black-bulb thermometer, may be greater in the former case than in the latter. This may be shown by a comparison of some available black-bulb thermometer readings. At Davos, Switzerland (altitude 1,559 meters), the average of the maximum black-bulb readings for three years was 53°.8 with the highest absolute maximum of 67° in 1910; at Manila, the maximum for the year 1910–1911 was 56°; at Helwan, Egypt, the highest observed was 70°.8 during a period of three years; at Alexandria, Egypt, the maximum was 57° during the same period. There are places on the edge of the desert, where the atmosphere is

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[1] A large number of photographs of the sun's spectrum taken in Manila and Baguio show that the ultra-violet is cut off at about the same point that other observers have noted in various parts of the world, namely, about 291 μμ.

especially clear and where reflected light is present in great proportion, that exceed these figures; for example, Cairo in May and August, 1909, showed a maximum of 79°.5, and Aswan Reservoir in June, 1910, of 81°. In contradistinction to these, we have another remarkably high black-bulb reading at high altitude in Leh, Thibet (altitude 3,517 meters), of 101°.7 with a shade temperature of 23°.9. Of course, these figures refer to the maxima only, and do not take into consideration averages or the shade temperature which may be high or low, but it is evident that the occurrence of days of extreme insolation is not so much a matter of altitude as situation, and that even in the Tropics we might come to averages decidedly lower than in some more northern temperate climates. It is obvious that in any one of the places mentioned a living body might encounter days in which it might be more heated by solar radiation than in the Tropics, and the only question would be whether the possibility of cooling, such as is brought about by lower atmospheric temperatures, low humidity, radiations, and other means, will compensate to avoid the effect of such insolation.

A body exposed to the sun absorbs a portion of the rays and reflects a portion of them, the most perfect absorber being a substance as nearly the ideal black as is possible. It loses the heat by radiation or convection (conduction), and while black bodies absorb radiations readily, they also radiate readily. It is a well-known fact that the ultra-violet rays are promptly fatal to all the lower organisms such as bacteria, amoebæ, and protozoa; the heat effect on them being much less, and only apparent in so far as above certain temperatures they cannot live. As we ascend higher in the order of animals, devices for regulating the loss of heat begin to appear, until in birds and mammals, they are so well developed that but very little variation in blood temperatures is observable in the most diverse conditions of life.

Since the study of the heat effect upon such organisms appeared to be the most promising, this was first undertaken by Dr. Hans Aaron[1] of the department of physiology of the University of the Philippines, in Manila, and later, by one of us in Baguio. The subcutaneous, rectal, and skin temperatures were accurately

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[1] *Phil. Journ. Sci., Sec. B., 6*, 101 (1911).

measured by means of thermocouples and a tangent galvanometer. Monkeys are naturally at home in the Tropics and we should suppose that these animals would best be able to stand the effects of sunlight. Their system of sweat glands[1] is not so highly organized as in man, and their physical heat regulation is to a much greater extent brought about by water evaporated by the lungs and mouth through increased respiration. Aron found the normal subcutaneous temperature of the animal in the shade to vary from 36°.6 to 38°; the rectal from 37°.9 to 39°.4. The subcutaneous temperature therefore is somewhat below the rectal. However, so soon as the animal is placed in the sun, the subcutaneous temperature rises above the rectal and remains so to the end of the experiment. Animals exposed to the sun without protection, or artificial means of lowering the temperature, died in Manila in from one hour to one hour and fifty minutes, both skin and rectal temperatures steadily rising, the maximum before death being 43.5° and 42.7° to 46.3° and 44.8°. In Baguio, at a higher elevation, the animals died in even a shorter time, although the atmospheric temperatures were lower. Entirely different results are obtained if the animals are shaded even by a small area of shade such as an umbrella or a board, all other conditions being similar, except that the direct rays are excluded. Under these conditions the skin and rectal temperatures never exceed 40° and the animals remain healthy. Similar results are obtained if the animals are exposed to the full insolation when care is taken to conduct away the excessive heat by means of a brisk current of air from a fan. Under these conditions the subcutaneous and rectal temperatures remain the same as in the animal if shaded, and the monkey remains perfectly well. In this last form of experiment the monkey is exposed to all of the rays of the sun, including those of shorter wave length. If the effects are to be attributed to the absorption

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[1] Aron, *Phil. Journ. Sci., Sec. B. 6*, 110, makes the statement that monkeys have no sweat glands. During the time at his disposal, as he was going on a long leave of absence, Aron did not investigate this question completely. Doctor Shaklee of the department of pharmacology, University of the Philippines, states that monkeys do have sweat glands. See also Blaschko, *Arch. f. mikros. Anat.* (1887), *30;* Wimpfelheimer, *Anat. Hefte* (1907), *34,* 492, Krause, Beiträge z. Kenntniss der Haut. d. Affen; Inaug. Dissertat., Berlin (1888); is not available. Sweat glands have been found by Mr. Clark of the department of anatomy, University of the Philippines, in the forehead, hands, feet, axillæ, and abdomian of our monkeys.

of the ultra-violet rays, then surely the animal is in the same condition to absorb the latter when no blast of air is present, and their effect should be apparent. On absorption a large portion of these rays is presumably converted to heat and conducted away as such, so that we can assume that the effects which are observed on exposing this animal to the sun, is one of the heat, and these conclusions are borne out at necropsies where post-mortem examinations give protocols clearly pointing to heatstroke. Monkeys enclosed in tight boxes with only the head exposed and placed in the full sun suffer no inconvenience, although the hair temperature on the scalp may reach 47°. The effects therefore are not due to penetration of the sun's rays to the brain. Of course, it must be understood that the monkey's skin is protected by fur, and is not sensitive to the irritating effects of the ultra-violet rays of the sun, as is the skin of a Caucasian, who, we know, if exposed to the sun, would be sunburned, whether in a strong blast of air or not. This latter effect is due to the ultra-violet portion of the spectrum, the rays of which are easily guarded against, and the skin can, in time, amply protect itself by pigmentation. Dr. Shaklee[1] has shown that monkeys, when exposed to the sun's rays for short periods daily, acquire a sort of immunity. After a few weeks' exposure they are able to remain in the sun for hours without ill effects. Experiments performed in Baguio[2] on rabbits gave remarkably conclusive and interesting results.

The rabbits exposed to the sun did not live so long as monkeys. White, grey, and black-haired rabbits were employed in the experiments, and it was found that the black died first, the grey next, while the white rabbits were able to withstand the exposure. The subcutaneous temperatures taken with thermocouples through small slits in the lower dorsal region usually do not rise so high as those in the monkey's before death. These results are particularly interesting in relation to the question of proper clothing for the Tropics, in showing the protective value of the white coat as opposed to the darker colors.

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[1] Results to be published in *Phil. Jour. Sci.*

[2] Gibbs, H. D.: The effect of sunlight upon men, monkeys, and rabbits, and a discussion of the proper clothing for protection. *Phil. Journ. Sci., Sec. A. 7*, No. 2 (1912).

EXPERIMENTS UPON HUMAN BEINGS

Experiments upon man are equally interesting. Here we have a subject with highly developed sweat glands, so that the means of heat regulation by evaporation are much more complete than in dogs, rabbits, or monkeys. Skin temperatures in this climate in the shade under normal conditions vary within the extreme limits of 31° to 34°, being higher over the muscular and fatty parts of the body than over bony structure lying close to the surface. Aron made a comparison of Malays and Americans and out of observations, 12 showed a slightly lower skin temperature for the Malay, the highest of all observations being 37°.4. In our experiments in Baguio, all subjects exposed to the sun showed higher skin temperatures than those obtained by Aron in Manila, and all were above that of the blood, even though the air temperatures were considerably lower than in Manila. The lighter colored skins reached maxima in a shorter time than the darker, and the darker finally attained maxima higher than those of the lighter color. The theory of protective value of the darker skins would seem to be somewhat nullified by these observations.

Comparisons between an American and two dark-skinned Igorots, in the first series, and between a Canadian, a Tagalog, and an American Negro in the second series, were made by temperature measurements taken over the level of the third dorsal vertebra, the fifth dorsal vertebra, and over the upper angle of the scapula. The shade temperatures first taken showed the average of the lighter skins to be considerably lower than the dark, in some cases the differences being so great as 3°.68, namely, 29°.8 for American and 33°.48 for Negro.

In spite of the fact that the American's temperature in the shade was, on the average, 2°.9 lower than the Igorot's, on moving into the sun the three subjects (2 Igorots and 1 American) reached, on the average, about an equal temperature near the maximum, in thirteen minutes for the American, and about thirty minutes for the Igorots. The final temperatures are decidedly against the Negro, slightly so against the Malay, and in favor of the Canadian and the American.

The rapid rise of the white skin is explained by the irritation of the sensory nerve-endings, nerve-endings in the vessel walls, or of the vessel walls themselves, producing a flushing of the skin due to a greater quantity of blood and a more rapid flow. This effect, absent in the dark-colored skins even though they do absorb heat more rapidly, results unfavorably for the lighter colors. A greater quantity of blood flows to the exposed parts of the body and is there heated, and moreover it has been shown that ultra-violet light converts oxyhemoglobin into methemoglobin. Preliminary experiments, upon rabbits exposed to the sun, have shown that in some cases methemoglobin can be detected in the blood before death. This work is only begun and more definite statements at this time are premature.

While the series of observations upon human beings is not extensive enough to be conclusive in comparisons of the white and dark races, they at least show that the adaptable mechanism for heat regulation possessed by human beings is sufficient to lower the temperature and protect the individual from such fatal effects as are observable in monkeys. One fact very strikingly appears from these measurements, namely, that the skin temperatures of all the subjects reach higher points in the sunlight at the high altitude of Baguio than they do in Manila, despite the lower shade temperature of the former place. It appears that the balance between absorption of heat on the side exposed to the sun and radiation from the shaded portion[1] of the body is against the dark skins and in favor of the lighter colors. On the other hand, with the white skin we have the phenomenon of sunburn and the resultant ill effects not obtained where there is the protection of pigmentation.

Chamberlain[2] has published the results of a series of observations in which he compared the relative resistance to the Philippine climate of blond and brunette types of soldiers, and he concludes that the evidence is conflicting and that from a consideration of the facts the blond is quite as well able as the brunette to withstand the climate.

Phalen[3] compared 500 troops in the Philippines dressed in orange-red underclothing with 500 dressed in white. The experi-

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[1] It very rarely happens that the area of the shaded portion of an animal body, exposed to the sun, does not greatly exceed that of the surface exposed.

[2] *Phil. Journ. Sci., Sec. B.* (1911), *6*, 427 (1911).

[3] *Ibid.* (1910), *5*, 525.

ment showed that the red underclothing added materially to the burden of heat upon the system and that the white underclothing of practically the same weight was superior in this respect.

Since the body is cooled by radiation and evaporation of moisture, it is evident that any clothing which interferes with these processes will materially add to the burden of the individual. The ideal condition would doubtless be that attained by an umbrella where the subject is constantly in the shade and the radiation and evaporation of perspiration are unobstructed. It is remarkable how instinctively, or otherwise, the native in the Tropics has adopted this form of protection. In many places, the workers in the fields will be found to wear practically no clothing and a large hat manufactured of various native fibers often so large as one meter in diameter. The nearer the white person can approach this condition, the more comfortable he will be in the Tropics, when the effects of sunlight alone are considered. The clothing should be white and so thin as possible to allow for unobstructed passage of air currents.

Relative humidity plays a most important part upon the influence of the various factors which go to make up climate in the Tropics. The higher the relative humidity, other things being equal, the less rapidly will evaporation take place and less complete will be the lowering of the temperature. As the lowering of temperature is brought about by the evaporation of sweat, it necessarily follows that those races with the best developed sweat glands will have an advantage. Mr. Elbert Clark[1] of the Department of Anatomy of the University of the Philippines has made an extended investigation of this subject. After many measurements on American soldiers, Philippine scouts, and persons of both color in civil life, he has come to the conclusion that the Malay possesses from twelve to fifteen per cent more sweat glands than the white. Measurements on Negroes are not yet complete enough to warrant a final statement, but the results show that the race has perhaps an excess of seven per cent. The few counts which have been made upon Negritoes show 26.82 per cent excess for adults and 67.54 for youths. Nothing can as yet be said concerning the relative capacity of the individual glands of the two races. In this

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[1] Results to be published.

respect then the Malay possesses a decided advantage over the white man, which the latter can only offset by seeking greater shade. Probable, injurious, or disagreeable effects attributed to tropical sunlight are caused by the evenness of the climate rather than by the difference of insolation as compared with other places. The monotony due to the absence of severe contrasts, such as are given by winters, has its effect. However, Chamberlain[1] investigated the systolic blood pressure and pulse rate in 6,847 readings and 1,489 individuals of varying lengths of residence in the Tropics, and he found that the pressures were little, if any, below those found in temperate climates. There was no progressive tendency for the pressure to increase or decrease with continued tropical residence up to a little over three years, beyond which point his observations did not extend. He concludes that the mean blood pressure for Filipinos during the period of fifteen to forty years of age does not differ from the pressure at the same age for Americans residing in the Philippines, for neither race is very materially below the figure to be expected of white men residing in temperate climate. Other investigators believe that the blood pressures are lower in the Philippines and do not think that all of Chamberlain's conclusions are entirely warranted by his data. Musgrave[2] states "there is a general lowering of the blood pressure in tropical climates and that this affects all classes and conditions of people. The normal blood pressure of the Filipino runs lower than average figures taken from temperate climates and runs much lower than the pressure in the same people while residing in temperate climates."

In conclusion, it must be pointed out that if individuals must be exposed to the sun, as in the case of troops on the march, they can be given adequate protection from the sun by light, preferably white, clothing and helmets, but it must be remembered that perspiration is a great factor in keeping the body normal under these conditions and that during exercise in hot weather much water is lost during the day. Some of the ill effects attributed to the sun are probably due to rapid loss of water from the system and

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[1] *Phil. Journ. Sci., Sec. B. 6*, 431 (1911).

[2] Musgrave and Sison: *Phil. Journ. Sci., Sec. B. 5*, 325 (1910). Further experiments now in progress, and results communicated by letter. These will be published shortly.

could be avoided if the individual were in a position to drink enough to preserve the equilibrium. If a supply of pure water is not present, the temptation to drink available water along the road may become irresistible, and sickness caused by infection from such a source may be attributed to the sun as a predisposing factor.

ABSTRACT

In this paper the action of sunlight upon a number of organic compounds, a comparison of sunlight intensities by means of a chemical photometer, and the influence of sunlight upon animals are described.

The coloration of various hydroxy benzenes is due to oxidation, the colored compounds in every case investigated being a quinone. Compounds of this class are not colored by sunlight in the absence of oxygen, that is in vacuo or in an atmosphere of indifferent gases. The coloration in the sunlight is characteristic of the presence of the so-called labile hydrogen atom. A fixation of the labile hydrogen atom and, in some cases, the hydrogen para to the hydroxyl group will reduce the activity of the compound and inhibit the formation of the color. Anilin will color in the absence of oxygen, the principal color compounds formed being azophenine, benzene, and ammonia.

A comparison of sunlight intensities has been carried on in Manila, Baguio, Kuala Lumpur, Khartoum, Honolulu, Tucson, Washington and Munich, by means of the chemical photometer, the unranyl acetate-oxalic solution. This solution is catalyzed by the ultra-violet and adjacent portions in the visible spectrum. The results show that, on clear days in any of the places mentioned, the rate of reaction is practically the same. An increase of reaction rate is noticeable at the higher altitude of Baguio. The evidence points to the conclusion that the normal sunlight intensities of various localities vary but slightly on clear days, while the horizontal intensities are, of course, subject to great variations. The conditions in various places affecting the rate of the reaction of the solution are therefore dependent upon atmospheric conditions, and, only to a slight degree, on situation.

Monkeys and rabbits exposed to the action of the sun's rays die

within a very short time, usually in less than one hour, with all evidences of sun stroke. Animals with dark-colored fur are more susceptible than those of the lighter colors. Black rabbits die first, grey rabbits next, while the white survive for the greatest length of time. The subcutaneous temperatures measured by means of thermocouples approach 50 before death.

The skin temperatures of men in the shade are below that of the blood, and, when placed in the sun, they rise rapidly above blood temperatures. The white skins rise most rapidly, but the darker colors finally attain higher maxima. The rapid rise of the white skin of an American and a Canadian is explained by the irritation of the sun's rays upon the sensory nerve-endings, nerve-endings of the vessel walls, and the vessel walls themselves, producing a flushing of the skin due to a greater quantity of blood and a more rapid flow. This effect is absent in the darker skins, the pigmentation of which is undoubtedly a protection.

The supposedly injurious effects of tropical sunlight have been attributed, in a large measure, to the action of the more refrangible rays of the sun's spectrum lying in the region of the violet and beyond in the ultra-violet, and to them have been attributed even grave morphologic changes sufficient to bring about permanent differences in the races of the human family. So far as this work has gone, it seems to develop that if the so-called actinic rays are injurious in the Tropics, they are also the same on clear days in other portions of the world.

Clothing for human beings for protection from the sunlight should afford the greatest shade without obstructing air currents carrying off evaporated moisture. The superiority of white over colored materials as a reflector of the sun's rays is demonstrated by the experiments with rabbits and a few temperature measurements under clothing. The ideal condition is attained by the shade of a white umbrella lined with green cloth and supplemented by as little clothing as possible. A broad brimmed, white, light-weight helmet, setting up and away from the head, is the best substitute for the umbrella. It is evident that the best protection from the sunlight is shade.

A REVIEW OF THE PROGRESS IN PHOTOCHEMISTRY SINCE THE LAST INTERNATIONAL CONGRESS

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Several excellent systems of classification of photochemical reactions have appeared within the last few years, of which the most important are those by Plotnikow[1] and by Weigert[2]. The former classification is based on equilibria relations, while the latter is based on energy changes.

Probably the most interesting photochemical effects observed have been those occurring in ultra-violet light. Berthelot and Gaudechon have investigated the action of ultra-violet rays on gaseous substances with special reference to polymerization phenomena[3], to oxidation effects[4] (formation of higher oxides of nitrogen and sulphur), the oxidizing action on cyanogen and ammonia[5] and the synthesis of formic acid. The function of chromophyls (chlorophyl, etc.) in the photosynthetic reduction of carbon dioxide in the leaves of plants, is explained by Tswett[6] with the hypothesis that chlorophyl changes polychromatic light to monochromatic, energy being stored up and released as luminescence, causing the change. The synthesis of carbohydrates from carbon dioxide and water, in the absence of chlorophyl, has also been effected by Berthelot and Gaudechon[7] and by Stoklasa and Zdobnicky[8]. The decomposition of sugar solutions with respect to the mechanism of photochemical reaction and the formation of plant principles has also been studied by Berthelot and Gaudechon[9]. Paul Mayer[10] has been unable to verify their

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[1] Zeit. phys. Chem., *77*, 472 (1911).
[2] Zeit. wiss. Phot., *10*, 1 (1911).
[3] Comptes. rendus., *150*, 1169 (1910).
[4] Comptes. rendus., *150*, 1517 (1910).
[5] Comptes. rendus., *150*, 1327 (1910).
[6] Zeit. phys. Chem., *76*, 413 (1911).
[7] Comptes. rendus., *150*, 1690 (1910).
[8] Chem. Ztg., *34*, 945 (1911). Bull assoc. chim. Sucr. dis. *29*, 26 (1911).
[9] Comptes. rendus., *151*, 395 (1910).
[10] Bioch. Ztg., *32*, 1 (1911).

results. Berthelot and Gaudechon have further done considerable work on the photolysis of complex acids by ultra-violet rays,[1] using uranium salts as photocatalyzers, and on the decomposition of alcohols, aldehydes, acids ketones and esters[2]. They have also studied the comparative action of ultra-violet light on straight chain and cyclic organic compounds, as well as upon some inorganic substances. Cyclic compounds, so long as they are unsaturated, are extremely stable toward ultra-violet light. They find that ultra-violet light is, as a rule, without action on aqueous solutions of metallic salts[3]. The nitrification of various substances[4] was investigated, with the interesting result that nitrites (and no nitrates) were always formed. As in the case of fermentation, nitrification is prevented by the presence of acids. The process of nitrification was found to be reversible. The carbohydrate sorbose has been synthesized by Inghilleri[5] from formaldehyde and oxalic acid, by long exposure to light. Condensations by ultra-violet light have also been observed by Pribram and Franke[6] and conversion of stable stereo-isomerides into labile modifications has been reported by Stoermer, Friederici, Braütigam and Neckel.[7] The hydrolysis of saccharose was studied by Bierry, Henri and Ranc[8], as well as the effect of ultra-violet light upon certain other carbohydrates. Massol[9] showed that soluble starch becomes hydrolyzed when its aqueous solution is exposed to ultra-violet radiations, and that the reaction products are dextrins and maltose. The hydrolysis was not due to the small amount of hydrogen peroxide formed. The action of ultra-violet light upon lactic acid and lactates was studied by Ganassini,[10] by Landau[11] and by Euler.[12] Ganassini showed that it is only the

[1] Comptes. rendus., *151*, 262 (1911).

[2] Comptes. rendus., *151*, 478 (1910); *153*, 383 (1911). See also Klinger Ann. *382*, 211 (1911).

[3] Comptes. rendus., *152*, 376 (1911).

[4] Comptes. rendus., *152*, 522 (1911).

[5] Zeit. physiol. Chem., *71*, 105 (1911).
Zeit. physiol. Chem., *73*, 144 (1911).

[6] Ber. *44*, 1035 (1911).

[7] Ber. *44*, 637 (1911).

[8] Comptes. rendus., *151*, 316 (1910). *152*, 535. 639 (1911). Comptes. rendus., Soc. biol. *70*, 900 (1911).

[9] Comptes. rendus., *152*, 902 (1911).

[10] Seduta Soc. med. chir. Pavia (1909).

[11] Comptes. rendus., *152*, 1308 (1911).

[12] Arkiv Kemi Min. Geol., *4*, 1 (1911).

1-acid which produces pyruvic acid. Bruner and Krolikowski,[1] in studying the inversion of maleic acid to fumaric acid, have shown that in the presence of traces of bromine and in sunlight the reaction is monomolecular.

That the diastatic activity of yeast, sucrase, commercial diastase and pancreatin, emulsin, pepsin, rennet, and catalyse (from pig) is diminished to a greater or less extent by exposure to ultraviolet light, has been shown by Agulhon.[2] Light of wave length exceeding 302.2 has practically no action on enzymes. A good résumé of the early work on the chemical action of light, particularly with reference to organic compounds, has been given by Ciamician.[3]

It has been known for some time that the chlorination of benzene, toluene and xylene[4] is inhibited by the presence of oxygen. Bruner and Lahocinski[5] find that the photobromination of toluene is similarly retarded. When toluene is brominated in the dark in dilute solution, substitution takes place in the side chain to the extent of 20 per cent at 10° and to the extent of 45 per cent at 25°. Bromination caused by photochemical after-effect takes place exclusively in the side chain. If the (carbon tetrachloride) solutions of bromine and toluene are separately exposed to light and then mixed, there is no after-effect. The greater the concentration of the solution on which the after-effect is to be studied, the less pronounced is the phenomenon. The after-effect may last for hours, depending on the amount of bromine used. After a lapse of twenty-four hours between the photobromination and bromination in the dark, there is no longer an after-effect. Cooling the mixture to the temperature of liquid air does not weaken the after-effect, but heating to 100° for two hours destroys it. Later,[6] the same investigators found that the after reaction is dependent upon the presence of oxygen during the photobromination, that it is of the autocatalytic type and is probably due to oxidation products of bromine.

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[1] Anzeiger Akad. Wiss. Krakau, Series A, 192 (1910).
[2] Comptes rendus., *152*, 398 (1911).
[3] Bull. Soc. Chim. (4), *3*, 1 (1908).
[4] Zeit. Wiss. Phot., *4*, 61 (1906).
[5] Anzeiger Akad. Wiss. Krakau, 265 (1909).
[6] Anzeiger Akad. Wiss. Krakau, 560 (1910).

Coehn[1] verified Thiele's[2] observation that ultra-violet light causes oxygen and hydrogen to unite and found that the gases unite almost completely, without explosion, at temperatures as high as 150°. The reverse reaction, the decomposition of water, occurs to some extent, the equilibrium not being altered by a change in temperature over the range of 150–800° C. The equilibrium was found to correspond with the thermal equilibrium obtained by Nernst and von Wartenberg for 1250°. Andreef[3] also confirmed Thiele's work and found that the velocity of the reaction is independent of the concentrations of the reacting substances, that it increases almost proportionately with the intensity of the light, and that the mean value of the temperature coefficient is 1.1. When the reaction is reversed, the final state of equilibrium is the same. With an increase in the intensity of the light, the equilibrium is shifted in the direction of dissociation.

Chapman and MacMahon[4], studying the interaction of hydrogen and chlorine in light, conclude that easily reducible gases are, in general, inhibitors of this photochemical reaction. Chapman and Gee[5] find that the photochemical interaction of chlorine and carbon monoxide is inhibited by small quantities of certain gases in a similar manner. Weigert[6] has shown that in glass vessels the equilibrium $COCl_2 \leftrightarrows CO + Cl_2$ is not displaced by the action of light in the neighborhood of 500°. Coehn and Becker[7] show, however, that in quartz tubes $COCl_2$ is decomposed by ultra-violet light even at room temperature, and chiefly by light of wave-lengths of less than 265.

Tian[8] has made the interesting observation that the decomposition of hydrogen peroxide by light is unimolecular, as it is when catalyzers are used, whereas the decomposition by heat is bimolecular. Coehn[9], studying the equilibria $SO_2 + O \leftrightarrows SO_3$, finds that neither reaction will take place in ultra-violet when the gases have been dried over phosphorous pentoxide. The photo and

[1] Ber. *43*, 880 (1910).
[2] Ber. *40*, 4914 (1907).
[3] Jour. Russ. Phys. Chem. Soc., *43*, 1342 (1911).
[4] Jour. Chem. Soc., *95*, 1717 (1909). *97*, 845 (1910).
[5] Jour. Chem. Soc., *99*, 1726 (1911).
[6] Ann. Physik, (4) *24*, 55 (1907).
[7] Ber., *43*, 130 (1910).
[8] Comptes. rendus., *151*, 1040 (1910).
[9] Chem. Ztg., *31*, 541 (1907).

thermal equilibria are not the same. The former is independent of the temperature (up to 800°).

The reaction between chromic acid and quinine in the light, originally studied by Goldberg[1], has been further investigated by Luther and Forbes[2]. Plotnikow[3] has studied the oxidation of iodoform by means of oxygen in monochromatic light, using an improved thermostat with constant saturation with oxygen. The reaction was found to be highly dependent on the nature of the solvent, on the wave-length of the light used and upon the various catalyzers employed. The same investigator has made the interesting observation[4] that all the photochemical temperature coefficients so far determined fall into three groups, the mean value of each group being 1.04±.03, 1.20±.03, and 1.39±.03, respectively (coefficient is determined for ten degrees). The suggestion is made that these regularities are due to three different types of electron configurations.

That those portions of the spectrum which are generally considered most active photochemically may have a retarding effect on certain photochemical reactions has been definitely shown by Trautz[5]. For example, in the case of the action of oxygen on ammoniacal copper bromide, red, green and yellow accelerate, while violet light retards the reaction. That the sensitiveness of Eder's solution is highly dependent upon and proportional to the amount of iron (invariably present as an impurity) in the solution, has been shown by Winther.[6] With increasing iron content, the sensitiveness maximum moves from the ultra-violet into the visible spectrum; therefore Eder's solution is not suitable for comparative actinometric measurements. A résumé of our knowledge of the relations between the absorption of light and the chemical constitution of organic compounds has been given by Ley,[7] who discusses the subject under the following heads: 1. absorption, 2. chromophore theory, 3. color and configuration, 4. bathochromic and hypochromic groups, auxochromes, 5. quanti-

[1] Zeit. Wiss. Phot., *4*, 95 (1906).
[2] Jour. Am. Chem. Soc., *31*, 770 (1909).
[3] Zeit. phys. Chem., *75*, 337 (1910)ff.
[4] Zeit. phys. Chem. *78*, 572 (1912).
[5] Jahrb. Phot. *23*, 57 (1909).
[6] Zeit. Wiss. Phot., *8*, 197, 237 (1910).
[7] Zeit. angew. Chem., *20*, 1303 (1907).

tative relations, influence of solvent, 6. extension of auxochrome theory, 7. rearrangement theory, change of color with salt formation (Hantsch) and 8. isorropesis.

Some interesting mechanical effects of ultra-violet light have been observed by Guntz and Minguin.[1] Gk *d*-Benzilidine camphor got warm, the faces became dull and showed etchings similar to those made by toluene, rock candy also became etched, turned yellow and yielded a yellow reducing substance. Various polymerizations and changes of allotropic forms were also observed.

That ultra-violet light accelerates the rate of change of plastic into rhombic sulphur, of vitreous selenium into the crystalline form, of amorphous barley sugar into crystalline, potassium manganate into potassium permanganate, the reaction between potassium permanganate and oxalic acid, the inversion of sucrose by acids, and the saponification of ethyl acetate by sodium hydroxide, has been observed by Pougnet.[2] The reversible photoreaction of sulphur has also been studied by Wigand[3], who finds that the equilibrium $S\lambda = S\mu$ is a true reversible photoreaction. The transformation by light in the precipitation of $S\mu$ from a sulphur solution was determined for various solvents.

Bates[4] finds that the insulating power of sulphur is decreased upon illumination by sunlight. Ebonite shows a slight effect of the same kind, but amber is not influenced. That the conductivity of certain liquid dielectrics is increased by ultra-violet light, has been shown by Szivessy and Schäfer[5] and by Byk and Borck.[6] Perman[7] has shown that canal rays, in air or in oxygen, have a strong oxidizing action. Many substances are decomposed by the action of canal rays, independently of the nature of the gas in which the rays are produced.

McKee and Berkheiser have shown[8] that water of crystallization may be affected by the action of light. Aniline-*p*-sulphonic acid loses its water of crystallization more readily when exposed to

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[1] Comptes. rendus., *152*, 372 (1911).
[2] Jour Pharm. Chim., (7), *11*, 540 (1910).
[3] Zeit. phys. Chem., *77*, 423 (1911).
[4] Le Radium. *8*, 312 (1911).
[5] Ann. Physik, *35*, 511 (1911).
[6] Ber. phys. Ges., *9*, 621 (1910); Jahr. Phot., *25*, 58 (1911).
[7] Jour. Chem. Soc., *99*, 883 (1911).
[8] Am. Chem. Jour., *40*, 303 (1908).

sunlight than when kept in the dark. It was shown that the phenomenon was not a temperature effect.

Two equations have been deduced by Winther[1] to express the velocity of a non-reversible photoreaction, one on the assumption that the velocity is proportional to the intensity of the light at each point of the reacting system, the other on the assumption that the velocity is proportional to the light absorbed. Comparison of the two equations shows that they are identical for monomolecular reactions, and since those photochemical changes heretofore investigated are all unimolecular, it is impossible to decide whether the velocity is determined by the absorbed light or not. According to Weigert[2], the velocity depends upon the absorption of light rather than upon the intensity of the incident light. This investigator further concludes that the law of mass action does not apply to photochemical reactions.

Bancroft,[3] in a series of nine articles appearing from April 1908 to April 1910, has revived a suggestion of Grotthus concerning the analogy between the action of light and electrochemical phenomena, and has given us interpretations of many photochemical reactions in the light of this hypothesis. Naturally, the suggestion of Grotthus has been greatly amplified, since our knowledge of photochemical reactions has increased enormously since 1818, the time the suggestion was made.

Schluederberg[4] has studied the chlorination of acetic acid, benzene and toluene, both photochemically and electrolytically, and has repeated many of Herschel's photochemical experiments electrolytically. A considerable number of new photoelectric effects have been described and considerable new evidence has been found for Bancroft's electrochemical theory of the action of light.

[1] Zeit. Wiss. Phot., *7*, 666 (1909).
[2] Zeit. Wiss. Phot., *7*, 273, (1909).
[3] Jour. Phys. Chem., *12*, 209 (1908) ff.
[4] Jour. Phys. Chem., *12*, 574 (1908).

THE EFFECT OF CHANGES OF COMPOSITION ON THE REDUCTION POTENTIALS OF DEVELOPING SOLUTIONS

By F. Austin Lidbury
Niagara Falls, N. Y.

In continuation of the work already described[1] it was decided to investigate the influence of the different constituents of a developer, and of their concentration, on the reduction potential. In the case of two standard formulæ for pyrogallol and hydroquinone the following measurements were obtained, all the potentials being given with reference to the value —.56v. for the normal calomel electrode:

		Grams per Liter	
Pyrogallol	8	8	8
Sodium Carbonate	20	20	20
Sodium Sulphite	..	20	20
Potassium Bromide	..	..	5
After			
48 hours	−.03	−.02	−.03
96 hours	−.04	.00	−.07
192 hours	−.04	.04	−.08

		Grams per Liter	
Hydroquinone	5	5	5
Sodium Carbonate	25	25	25
Sodium Sulphite	..	25	25
Potassium Bromide	..	..	1
After			
24 hours	−.03	−.09	−.08
96 hours	−.16	.06	.05
216 hours	−.02	.13	.14

Here again, as in the case of the formulæ used in the dilution experiments (1. c.) the potential values of hydroquinone are con-

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[1] "The Influence of Dilution on the Reduction Potentials of Developing Solution," Congress, Photochemical Section.

siderably higher; but it will be noticed that this occurs only after the addition of sodium sulphite. A similar but not so marked increase is shown in the case of pyrogallol. The addition of bromide does not appear to affect the potential of the hydroquinone developer, but has a marked affect upon that of pyrogallol. In order to study these conditions more closely, a series of measurements was planned in which the effect of the concentration of every ingredient of a developer upon its reduction potential would be studied. I was unable, however, to carry this further than the investigation of the effect of sodium carbonate and sodium hydrate on hydroquinone in the absence of other constituents. The results are given below.

	Grams per Liter			
Hydroquinone	5	5	5	5
Sodium Carbonate	125	25	5	1
After				
1 hour	−.18	−.20	−.27	−.35
24 hours	−.04	.07	−.02	−.10
72 hours	−.05	−.02	−.03	−.09
144 hours	−.04	−.02	−.01	−.04

There appears in this case to be no significant difference in the constant values obtained, though a considerable difference in the rates at which the values become constant.

	Grams per Liter			
Hydroquinone	5	5	5	5
Sodium Hydrate	25	5	1	.2
After				
1 hour	−.20	−.10	−.27	−.24
18 hours	−.02	.13	.00	−.13
42 hours	.05	.08	.00	−.12
66 hours	.03	.06	−.02	−.11

Here is observable a considerable initial increase followed by a slow decrease to a constant value in the case of solutions strong in sodium hydrate. It appears to be most marked in a solution containing approximately 5 grams per liter each of hydroquinone and sodium hydrate. This phenomenon was observed in a number of series of measurements of solutions approximating this composition. I have been unable to find a satisfactory explanation. It may or may not be significant that Kenneth Mees, in some recent work on the fogging power of developers, finds certain peculiarities attaching to a developer of approximately the same composition.

	Grams per Litre						
Hydroquinone	44	22	11	5.5	2.7	.14	.7
Sodium Hydrate	4.4	4.4	4.4	4.4	4.4	4.4	4.4
After							
1 hour	−.20	−.14	−.06	−.07	−.15	−.18	−.19
20 hours	−.13	−.05	.00	.08	.04	.04	.06
48 hours	−.11	−.03	.01	.07	.03	.03	.03
168 hours	−.11	−.06	−.02	.04	.02	.00	.01

Here again the increase and subsequent decrease with time, referred to above, are to be noted in certain strengths. Another fact not easy to explain is the decided lowering of reduction potential as the concentration of hydroquinone is increased beyond a certain point.

SUMMARY

1. The addition of sulphite to a developer consisting of sodium carbonate and hydroquinone or pyrogallol increases the reduction potential; the effect of the further addition of bromide was to lower it in the case of pyrogallol only.
2. The reduction potential of a developer consisting of hydroquinone and sodium carbonate is not affected (after constant values have been attained) by wide variations in the concentration of the carbonate.
3. The reduction potential of a developer consisting of hydroquinone and sodium hydrate increases with increasing concentration of the sodium hydrate up to 2½%.
4. The reduction potential of a developer containing 4.4 grams per liter sodium hydrate and varying quantities of hydroquinone decreases with increasing hydroquinone concentration beyond 5 grams per liter.
5. The reduction potential of a developer of composition approximating 5 grams per liter hydroquinone and 5 grams per liter sodium hydrate first increases rapidly with time and subsequently decreases slowly to a constant value.

THE INFLUENCE OF DILUTION ON THE REDUCTION POTENTIALS OF DEVELOPING SOLUTIONS

By F. Austin Lidbury
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This paper presents the results of progressive dilution on the potential of the single electrode: platinised platinum — developing solution in the case of four developers of standard composition. The method employed has been described.[1]

All the potentials are given with reference to the value −.56v. for the normal calomel electrode.

Hydroquinone:	Grams per Liter
Hydroquinone	4.5
Sodium Sulphite	12.5
Potassium Bromide	1.1
Caustic Hydrate	4.5

After	Full Strength	¼ Strength	$\frac{1}{16}$ Strength	$\frac{1}{64}$ Strength
1 hour	−.02	−.11	−.20	−.36
18 hours	.16	.08	−.11	−.20
24 hours	.21	.13	−.10	−.19
42 hours	.19	.17	−.08	−.17

Metol:	Grams per Liter
Metol	16
Sodium Sulphite	62
Sodium Carbonate	65
Potassium Bromide	2

After	Full Strength	¼ Strength	$\frac{1}{16}$ Strength	$\frac{1}{64}$ Strength
1 hour	−.15	−.20	−.20	−.29
4 hours	−.13	−.17	−.13	−.22
24 hours	−.10	−.15	−.17	−.20
45 hours	−.07	−.14	−.17	−.23

[1] "On the Measurement of Reduction Potentials of Developers," this Congress, Photochemical Section.

Amidol:	Grams per Liter
Amidol	5
Sodium Sulphite	30

After	Full Strength	¼ Strength	$\frac{1}{16}$ Strength	$\frac{1}{64}$ Strength
1 hour	−.13	−.18	−.23	−.30
20 hours	−.12	−.14	−.20	−.29
44 hours	−.09	−.10	−.14	−.29

Rodinal:

After	4% Sol.	1%	.25%	.06%
2 hours	−.20	−.25	−.33	−.50
7 hours	−.17	−.20	−.23	−.36
22 hours	−.18	−.20	−.22	−.33
48 hours	−.16	−.18	−.24	−.32

It should be mentioned that these measurements were taken before the persistent effect of time was fully realized; and it may be that constant values are in some of the cases not yet attained. Further extensions of the degree of dilution resulted in an increasing steepness of drop of the potential curve; but, at these concentrations, the amount of active reducing agent is so small that in spite of the use of freshly distilled water it is difficult to eliminate the possibility of significant oxidation through air dissolved during the preparation and handling of the solutions. In general the values of all dilutions practically employed for development range from −.2 to 0. The hydroquinone developer forms an exception, the value of the full strength developer attaining .2 v. On the whole, the measurements do not lend much support to the assumption of a parallelism between reduction potential and developing power. Hydroquinone for instance is not usually considered more energetic than metol; and any one familiar with the enormous difference in practical development between a 4% solution of rodinal and a 1% solution of rodinal must be forced to admit that, to whatever these differences are due, it is certainly not the effect of dilution on the reduction potential.

SUMMARY

The potential of the single electrode: platinised platinum-developing solution was measured for Hydroquinone, Amidol, Metol and Rodinal developers of standard composition and of the same diluted to 1-4, 1-16 and 1-64 strength. No regularities are traceable between the developing peculiarities of the solutions and their reduction potentials.

ON THE MEASUREMENT OF REDUCTION POTENTIALS OF DEVELOPERS

By F. Austin Lidbury
Niagara Falls, N. Y.

It has been rather fashionable in certain quarters to ascribe the peculiarities of different developing solutions (both as regards the different quality of their action upon the same photosensitive system and also as regards the action or non-action of the same developing solution upon different photosensitives systems) to the reduction potentials of these solutions. The underlying hypothesis has had the advantage that, owing to the absence of a systematic investigation of these reduction potentials, it has been possible to "explain" all manner of peculiarities of development by its aid without coming into disastrous conflict with experimental facts. Since, however, the measurement of the single electrolytic potential (Pt. platinised-solution) affords a usually easy and reliable means of comparing the "reduction potential" of different solutions, it appeared desirable that something should be done to provide measurements by which theoretical speculations along the lines above referred to could be checked. Although the writer has found it impossible to carry this work very far, some of the results obtained are sufficiently interesting to make their publication desirable and the work at any rate constitutes the first step in a systematic investigation of the question. The author is indebted to Prof. Wilder D. Bancroft for suggesting the investigation.

The actual measurement of the potential differences Pt.—developer has presented certain difficulties. The first experiments, made with Rodinal, showed a progressive increase in the readings, rapid at first. This continued for such a long period that it was obvious that in order to avoid oxidation the measurements would have to be carried out in a closed cell; and consequently a cell somewhat of the type of construction described by Wilsmore[1] was afterwards employed. In such a cell the bottle can be com-

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[1] Wilsmore: Zeit. Elektrochemie, *10*, 685, Fig. 161 (1904).

pletely filled and measurements taken at any time over a prolonged period without disturbing the contents of the cell itself or exposing them to atmospheric oxidation. In order to minimize the effect of diffusion potentials a saturated solution of potassium nitrate was inserted between the cell and the calomel electrode. The e.m.f. of this combination was measured against a cadmium cell by the usual compensation method with a Lippmann electrometer.

In general it was found that the potential of the single electrode steadily increased in almost all cases, the increase diminishing with time, and the values attaining approximate constancy after periods which varied from one or two days to one or two weeks according to the solution under investigation. Ultimately, in order to save time, a number of these cells were constructed and measured simultaneously. This arrangement was particularly useful in investigating the effects of dilution and of the progressive change in concentration of some one constitutent; since occasionally it would be found that the readings on one of the series of cells would "lie off the curve." The reason for this is not clear; since the fact was not altered by short-circuiting the combination, nor did the same cell or cells exhibit this tendency in different experiments; on the other hand a repetition of experiments in which these irregularities occurred proved them to be irregularities merely. This circumstance resulted in the adoption, for the later experiments, of duplicate cells for each solution investigated. In the case of a developing solution containing hydroquinone 5.5 grams per liter and sodium hydrate 4.4 grams per liter, a very strong increase in the potential during the first few hours was followed by a decrease which persisted for a considerable number of days. It appeared that this might be due to one of several causes:

(a) Accidental oxidation.
(b) A reaction catalysed by platinum.
(c) Adsorption changes at the electrode.
(d) Action of time pure and simple.

In order to distinguish if possible between these, a solution of the given composition was sealed for about three weeks (A); another portion of the same solution was sealed for the same period with platinum black (B). These solutions were used in two cells, a third being filled with freshly made solution of the same composition (C), and a fourth with freshly made solution to which a small quantity of silver bromide was added (D). The values found were as follows:

Calomel normal electrode = −.56*v*.

After	A	B	C	D
1 hour	.01	.04	−.13	−.13
3 hours	.02	.05	.06	−.01
5½hours	.02	.05	.24	−.15
6½hours	.02	.04	.24	−.15
23 hours	.02	.04	.17	−.07
47 hours	.02	.04	.05	−.03
72 hours	.02	.04	.04	−.01
168 hours	.02	.04	.04	.01

The final values are constant within a few centivolts; and it is clear from the readings that whereas the variations with time are considerably affected by other conditions the final constant values are attained as the result of the practical equilibrium of some reaction proceeding in the solution itself. In any measurements therefore in which the change with time is not a factor of interest, work will be greatly facilitated by making up and sealing the solutions to be investigated for some time prior to the measurements.

The influence of temperature was investigated, but it was found that the difference brought about by varying the temperature from 2° C. to 44° C. amounted to only two centivolts.

SUMMARY

1. The single potential: platinised platinum — developing solution varies in general considerably with the time elapsed since the preparation of the solution.
2. This variation appears to be due to the progress of reactions within the solution, and decreases with time.
3. To obtain the constant final values, solutions should be stored two or three weeks after preparing or diluting.
4. Duplicate cells should be employed and results in which both cells do not agree discarded.

THE ELECTRO POTENTIALS OF CERTAIN PHOTOGRAPHIC DEVELOPERS AND A POSSIBLE EXPLANATION OF PHOTOGRAPHIC DEVELOPMENT

By J. Howard Mathews and Floyd E. Barmeier
Univeristy of Wisconsin, Madison, Wis.

The experimental work recorded in this paper was undertaken with the idea of ascertaining, if possible, whether there might not be a relation between the reducing power of photographic developers and the magnitude of their electro potentials.

In the measurements to be described a number of possible methods of procedure are obvious, since the developer is a mixture whose various components can be varied at will. We chose to limit ourselves for the present to the study of the effect produced by varying the concentration of the different ingredients of a few only of the numerous developers in common use.

The method of measurement of the single potential was that commonly used—the Poggendorf compensation method—with the calomel half cell and a Clark cell as a standard. The half cell was made up with great care, pure chemicals and redistilled mercury being used. Attempts to use silver as the electrode in the developer were not successful as the metal was attacked. Platinum electrodes, coated with platinum black, were therefore used, since these suffered no change.

The sodium sulphite used was Merck's C. P., and was found to contain 91% of sulphite, the remainder being sulphate. The sodium carbonate used was Baker's Analyzed. The metol, adurol, and amidol were made by Hauff. The hydrochinon was from Merck, and the dianol from Lumiere, while the edinol and eikonogen were of Baeyer's make.

Our first thought was to measure only the single potentials of numerous developers, changing the constituents and the concentration as desired. It was soon found, however, that the developers oxidize very rapidly, with an accompanying change in electro potential, and that these changes were really more important than the initial electro potentials. We thereupon decided to determine the rate of oxidation of various developers, allowing only a very limited supply of air for this purpose. The form of apparatus used is shown in the accompanying sketch. The capacity of the cell was about 100 cc. The trap at the side, which was filled with a very strong alkaline solution of pyrogallic acid, prevented entrance of oxygen. The electrode was placed near the side tube to reduce the resistance, and the bore of the stopcock was very large for the same reason.

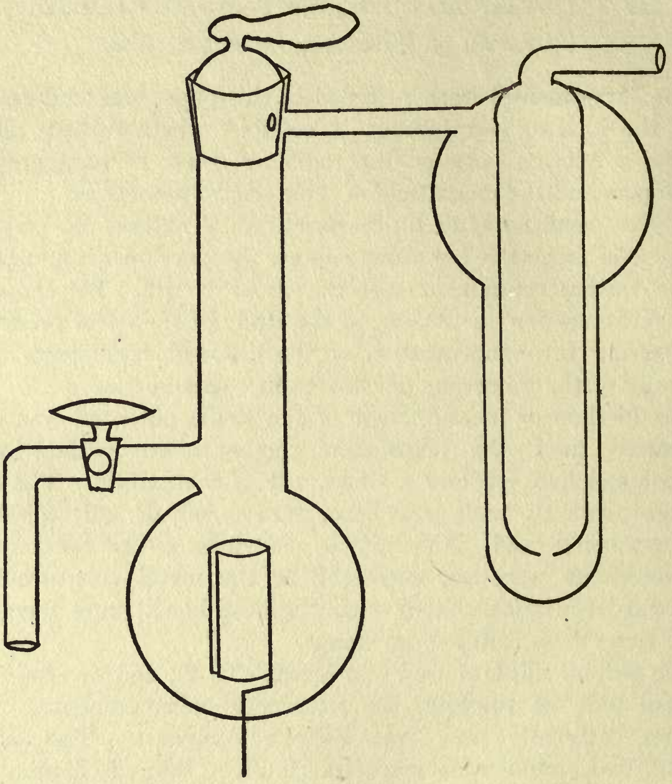


FIGURE 1

The materials for the solution were weighed out, quickly mixed and drawn into the apparatus before appreciable oxidation could take place. It was observed that oxidation proceeded at about the same rate no matter whether the tube was quite full or not. Separate experiments, in which the solutions were made up from oxygen free water in a vacuum, showed that the oxygen contained in the water was largely responsible for the oxidation. In the solutions so prepared there was not only no oxidation, but there was no change in the electro potential.

The first solution investigated was one containing 1 gram of edinol and 5 grams of sodium carbonate in 100 cc. of solution. The oxidation in this case was very rapid and the experiment was continued for 70 minutes only. In this time the potential rose from 0.830 to 0.952 and, as can be seen from Plate I, it increased more rapidly with increasing time. This change in potential was evidently due to the oxidation of the edinol. Solution No. 2 consisted of 1 gram of edinol and 5 grams of sodium sulphite in 100 cc. of solution. This solution oxidized much more slowly than the first, where the carbonate was used, the single potential changing only from 0.742 to 0.846 in a period of four days. The oxidation in this case was more rapid at first than later on, as is shown by the curve.

Solution No. 3 contained 5 grams of sodium sulphite in 100 cc. of solution, no edinol being present. The curve for this solution is practically the same in shape as that produced from solution No. 2. The single potential of the solution was lower, however, thus showing that the edinol raises the single potential. It is interesting to note that the solution containing edinol and sodium sulphite and that containing sulphite only oxidized in so nearly the same manner. This seems to show that in developers it is not the organic reducing agent which is oxidized, but instead it must be the sodium sulphite, and that the part played by the organic reducing agent is only that of inciting the action of the sodium sulphite on the plate. That it is not the edinol which is oxidized can be shown by the way the curve of oxidation of edinol, solution No. 1, runs, which is exactly opposite to the way curve No. 3 runs. Experiment No. 4 was simply a check run on No. 3, and the results obtained were the same.

In solution No. 5 we have 1 gram of edinol, 3 grams of sodium

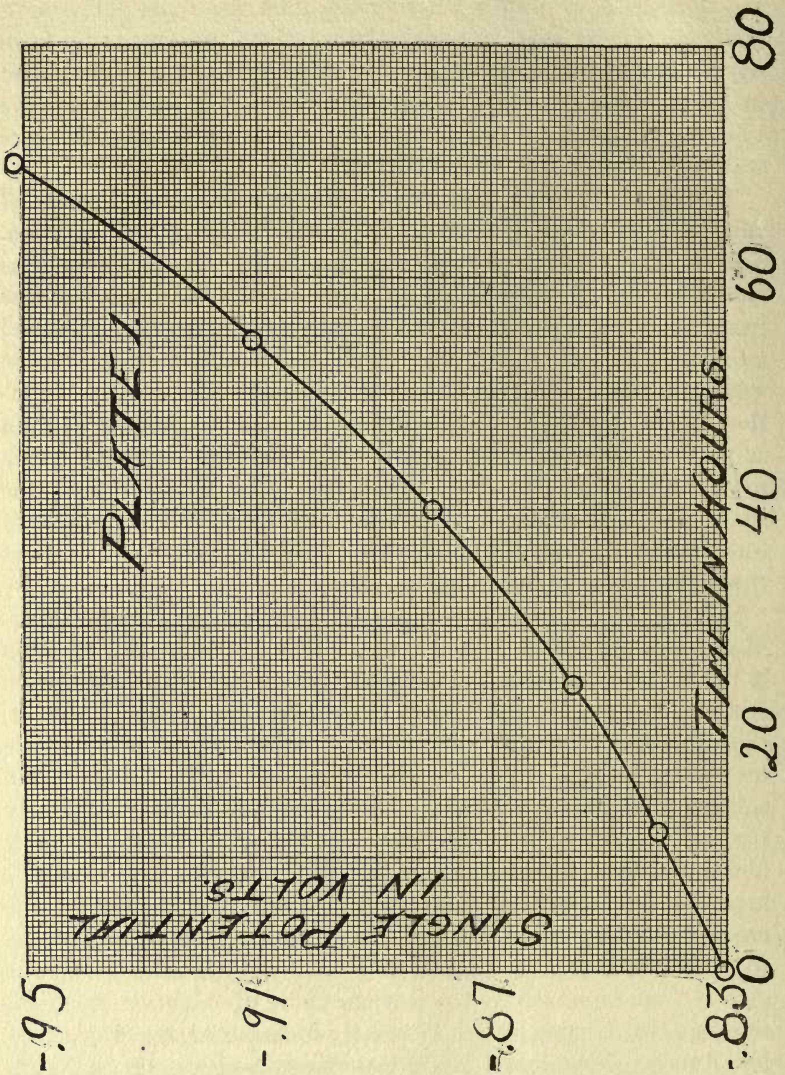


PLATE I.
SINGLE POTENTIAL IN VOLTS.
TIME IN HOURS.
0
20
40
60
80
-.83
-.87
-.91
-.95

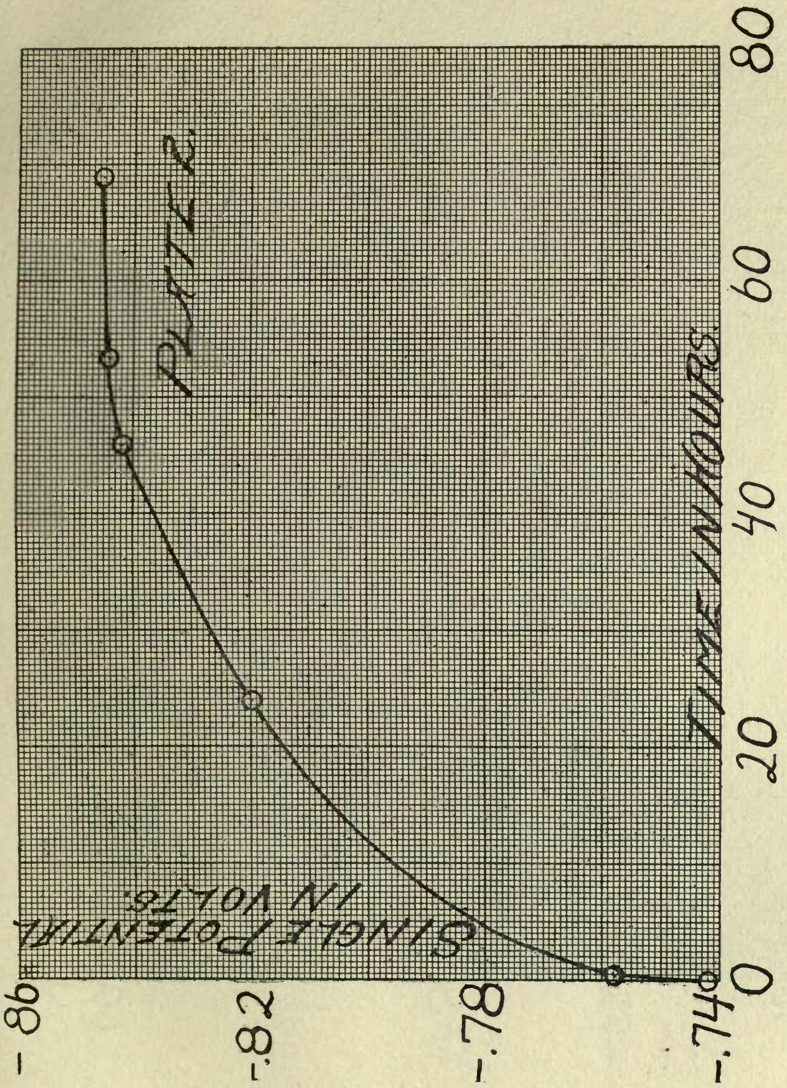


PLATE 2
SINGLE POTENTIAL IN VOLTS
TIME IN HOURS
0
20
40
60
80
-.86
-.82
-.78
-.74

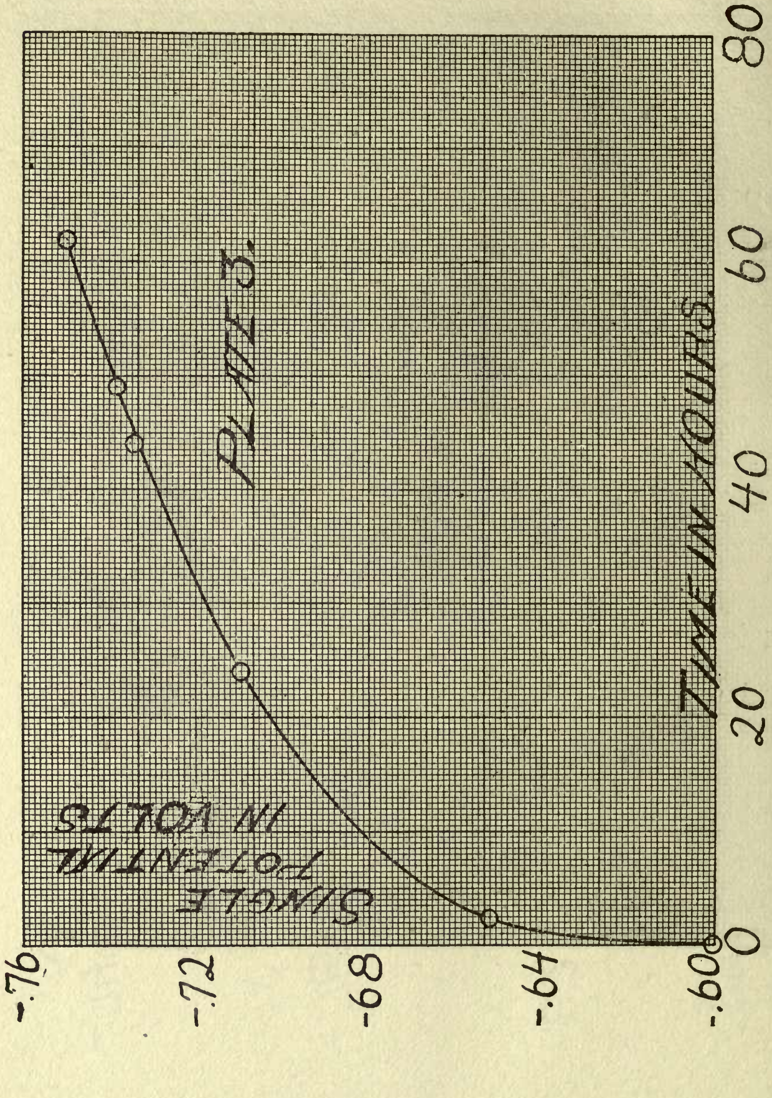


PLATE 3.
TIME IN HOURS.
0
20
40
60
80
SINGLE POTENTIAL IN VOLTS
-.76
-.72
-.68
-.64
-.60

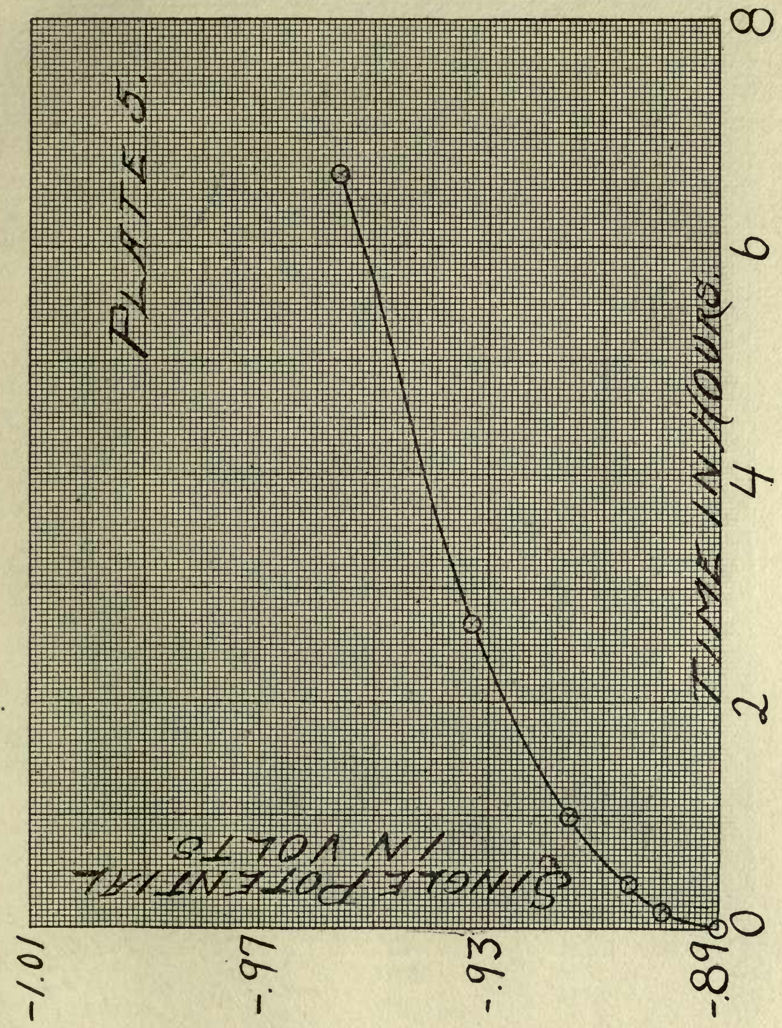


PLATE 5.
TIME IN HOURS
0
2
4
6
8
SINGLE POTENTIAL IN VOLTS.
-.89
-.93
-.97
-1.01

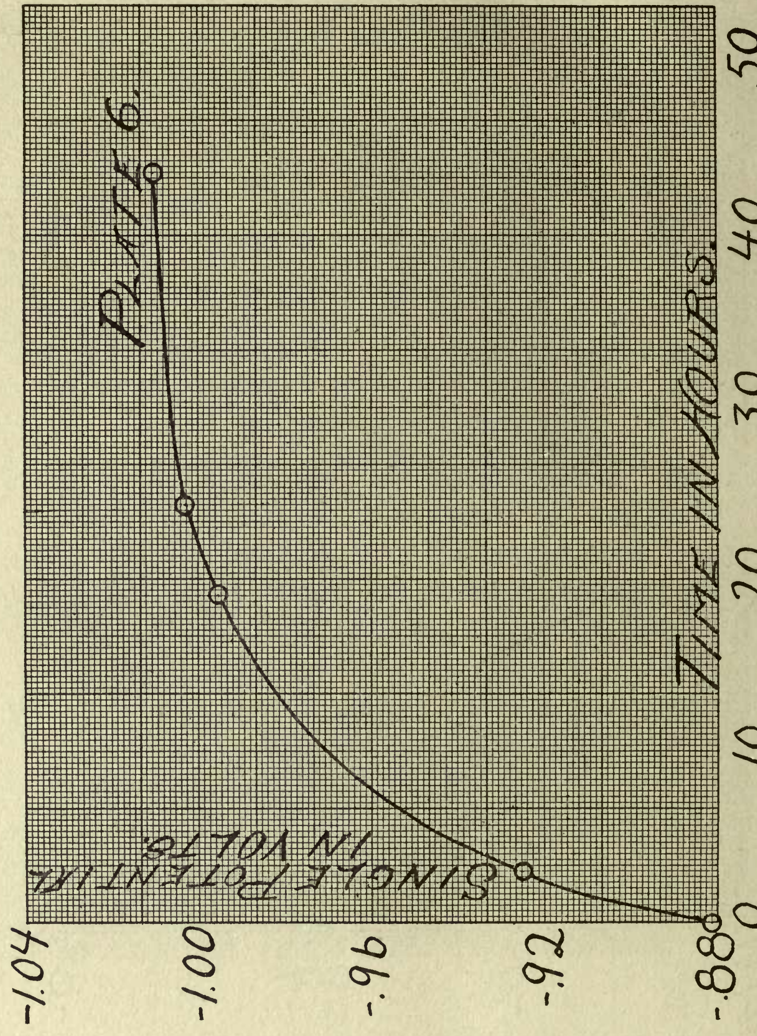


PLATE 6.
TIME IN HOURS.
0
10
20
30
40
50
SINGLE POTENTIAL IN VOLTS.
-1.04
-1.00
-.96
-.92
-.88

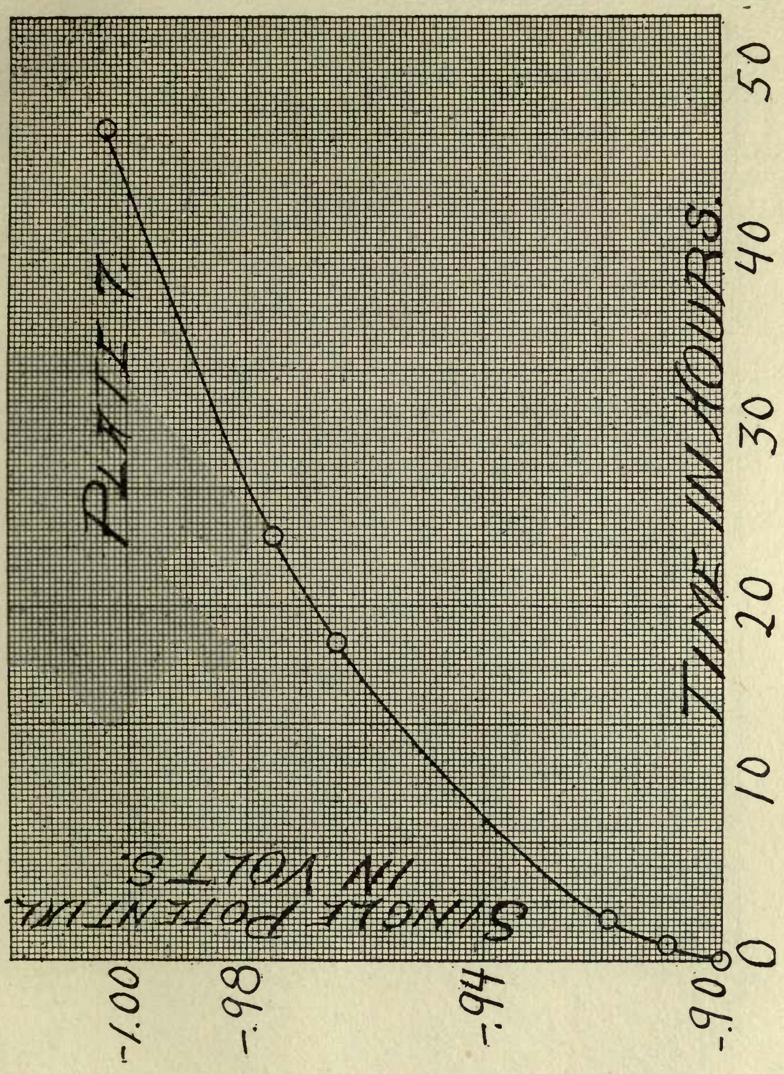


PLATE 7.
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS.
0
10
20
30
40
50
-.90
-.94
-.98
-1.00

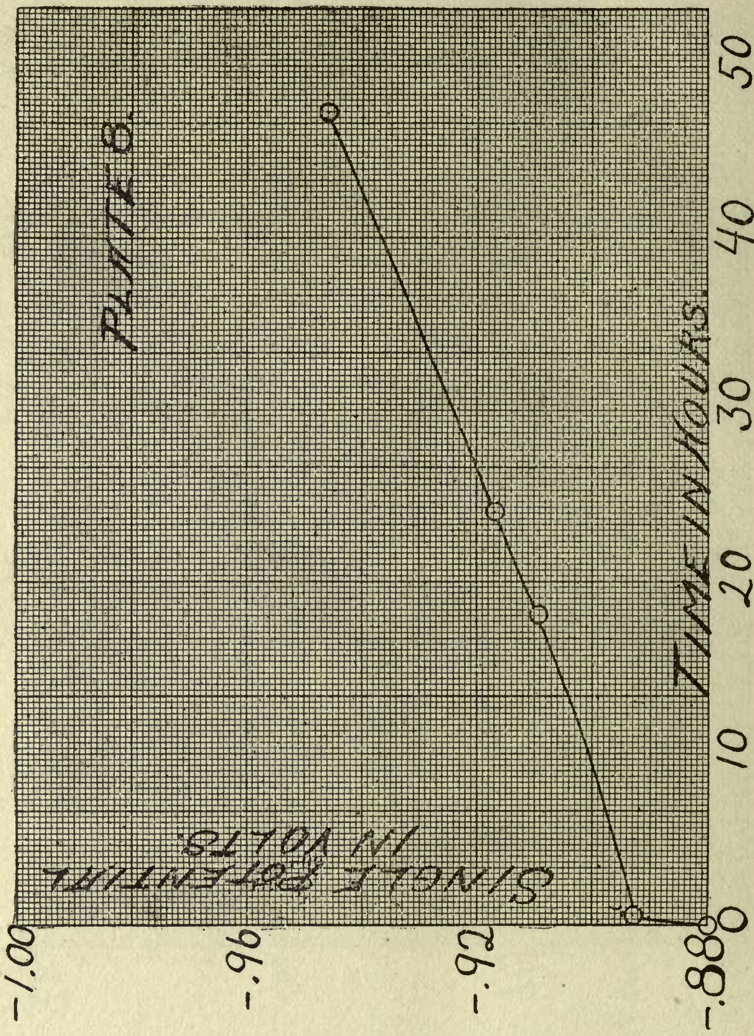


PLATE 8.
TIME IN HOURS.
0
10
20
30
40
50
SINGLE POTENTIAL IN VOLTS
-1.00
-.96
-.92
-.88

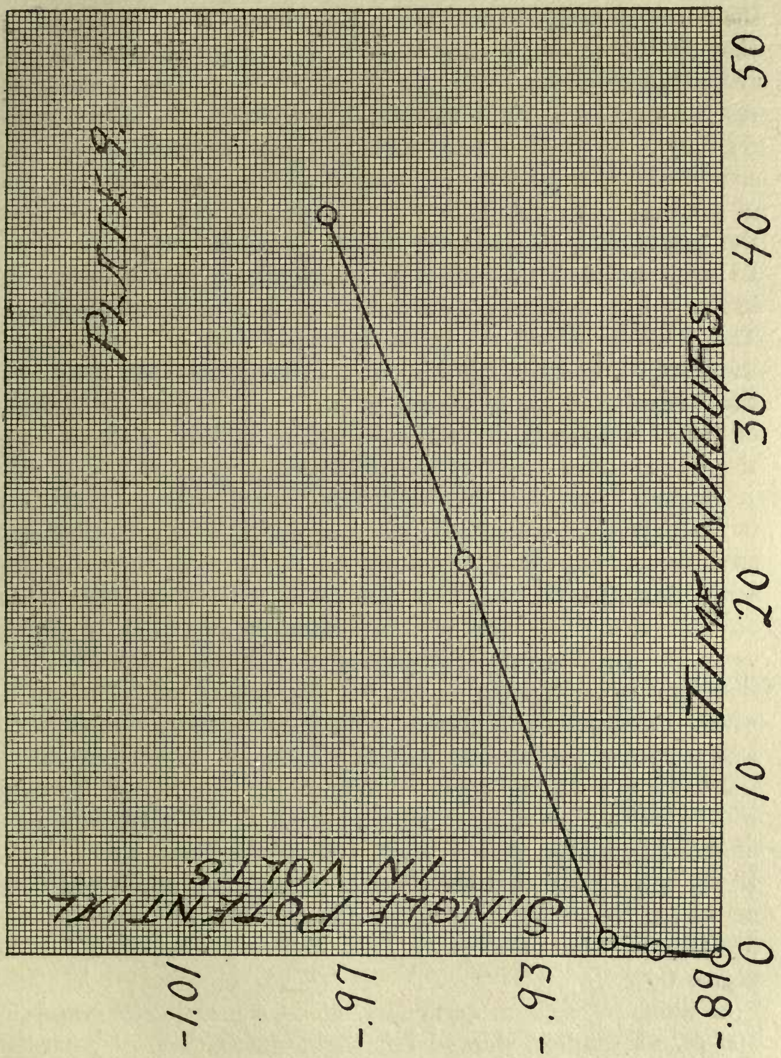


PLATE 9.
TIME IN HOURS
0
10
20
30
40
50
SINGLE POTENTIAL IN VOLTS
-.89
-.93
-.97
-1.01

sulphite, and 6 grams of sodium carbonate in 100 cc. of solution. It will be noted that the initial value of the single potential is higher, being 0.89 compared to 0.60 for Experiment No. 3. From the correspondingly high value in Experiment No. 1 it is evident that the sodium carbonate tends to raise the potential. Curve No. 5 runs similarly to Nos. 2, 3 and 4, except that it does not reach a maximum value as soon, but continues to oxidize more regularly. In solution No. 6 we have 1 gram of edinol, 5 grams of sodium sulphite, and 5 grams of sodium carbonate in 100 ccs. of solution. The curve for this is similar to No. 5, except that the oxidation proceeds more nearly proportional to the time. In solution No. 7 the developer was made up just the same as in No. 6, but with the addition of 0.5 gram of potassium bromide. This addition raised the initial potential slightly, and changed the trend of the curve, showing a retarding effect upon the oxidation. In solution No. 8 the same solution as No. 6 with the addition of 1 gram of potassium bromide was used. In this case the retardation of oxidation was very marked indeed.

The well-known fact that potassium bromide acts as a restrainer in the developer evidently is to be explained on electro-chemical grounds. It has also been known for considerable time that the other bromides do not have the same restraining effect upon development. The effect produced upon the potential by adding equimolecular amounts of sodium and ammonium bromides was therefore tried. In solution No. 9 0.85 grams of sodium bromide, which corresponds to 1 gram of potassium bromide, was added to a developer of the same composition as No. 6. The curve shows that oxidation was not retarded to anything like the extent found with potassium bromide. Similarly, in solution No. 10, 0.8 grams of ammonium bromide were used, with results like those in No. 9. It will be observed that the effect of potassium bromide was very marked indeed. For weaker solutions of bromide, such as are actually used in development, the differences would differ in degree only.

Solutions of sodium carbonate, alone containing 5 grams in 100 cc. of solution showed but slight fluctuations of potential upon standing for several days. The same was true for neutral solutions of edinol.

The preceding experiments were all made in the same apparatus, so that the amount of inclosed air and the surface exposure to the air were the same in each case. The distilled water from which the solutions were made had remained exposed to the air for some time so that the oxygen content was practically constant. Separate experiments made with boiled water showed this precaution to be necessary, as the oxidation was slower and more irregular in those solutions from which the oxygen had been removed by boiling.

Several other pieces of apparatus of practically similar construction, but of different dimensions, were tried with the idea of making possible a greater number of experiments, but it was soon found that the rate of oxidation in the different cells was not the same, due to differences in the amount of contained air and in the surface exposure. For this reason only those experiments which were made with the same piece of apparatus have been described in the preceding paragraphs.

The experiments now to be described were performed mainly to determine the differences in the initial potential and the behavior upon free oxidation of various developing solutions, so the measurements could be (and were) made in different cells, similarly constructed, but with free exposure to the air, in which case the form of apparatus naturally did not affect the result. The solutions were, in most cases, those recommended by the makers of the developer as the best formula for general work.

In solution No. 11 and No. 12 the metol content was kept the same and the amounts of sulphite and carbonate varied. It is interesting to note that the results were exactly opposite to those obtained with edinol (see curves). In the solution having the most carbonate the potential was lower than in the one with the greater amount of sulphite. In the case of edinol the opposite was true, *i.e.*, the carbonate tended to raise the potential. In the rate of oxidation the results are also opposite, *i.e.*, the curve for the solution with the greater amount of sulphite is more nearly linear than that with the greater amount of carbonate.

In solutions Nos. 13, 14, and 15 the effect of changing the relative amounts of metol and hydrochinon was tried, keeping the other constituents constant. In all cases the rate of oxidation was

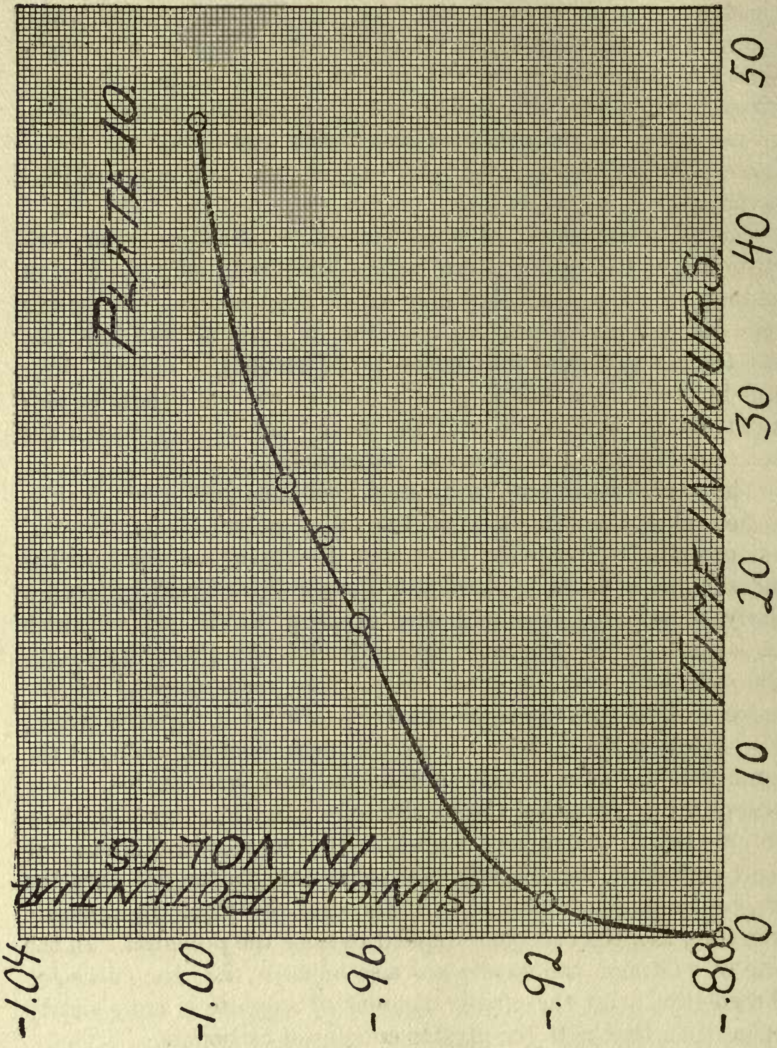
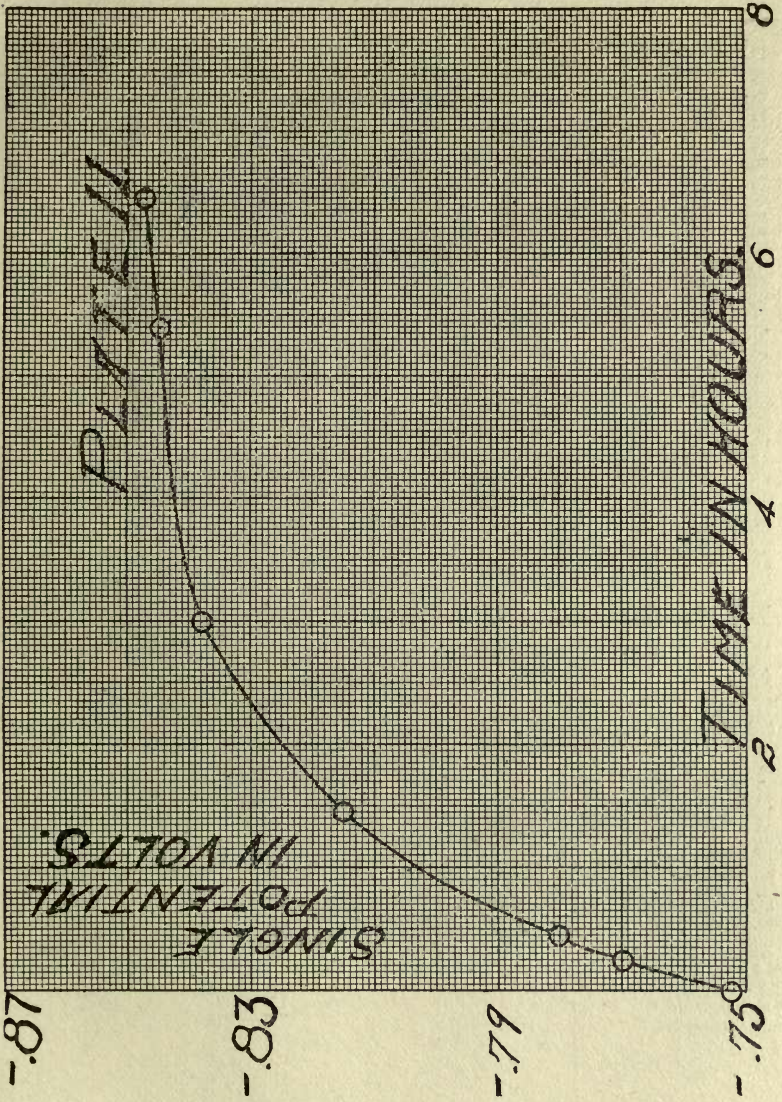


PLATE 10.
TIME IN HOURS.
0
10
20
30
40
50
SINGLE POTENTIAL IN VOLTS.
-1.04
-1.00
-.96
-.92
-.88


PLATED
TIME IN HOURS
SINGLE POTENTIAL IN VOLTS
2
4
6
8
-.87
-.83
-.79
-.75

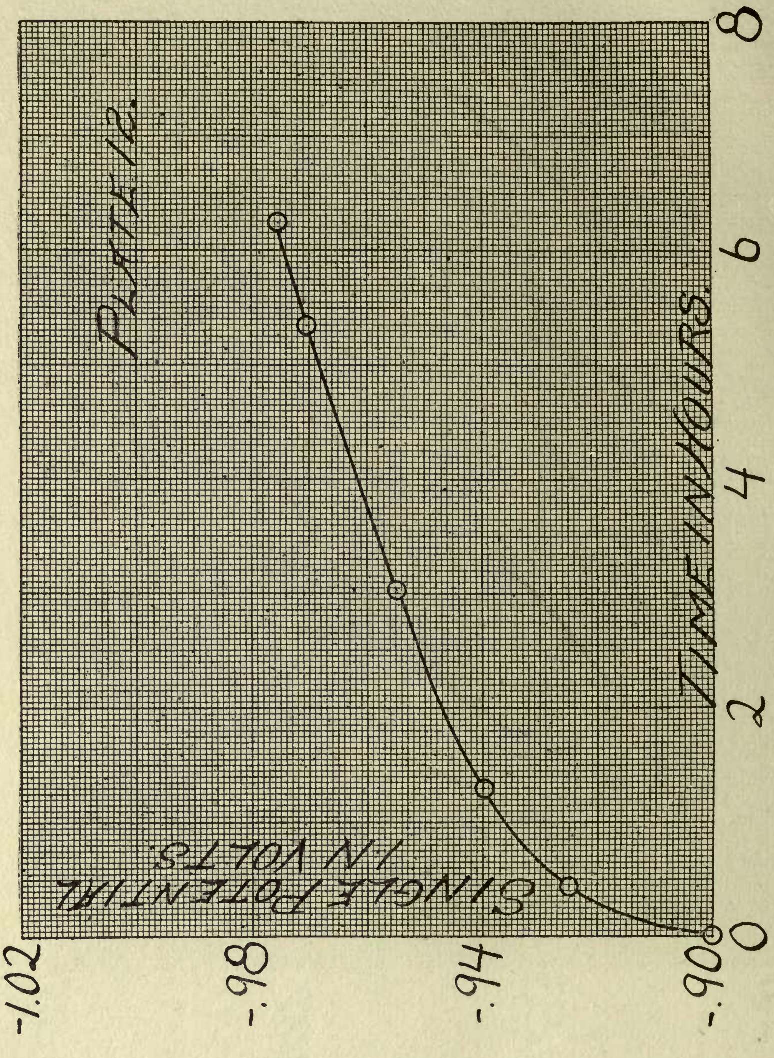


PLATE 12.
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS.
0
2
4
6
8
-.90
-.94
-.98
-1.02

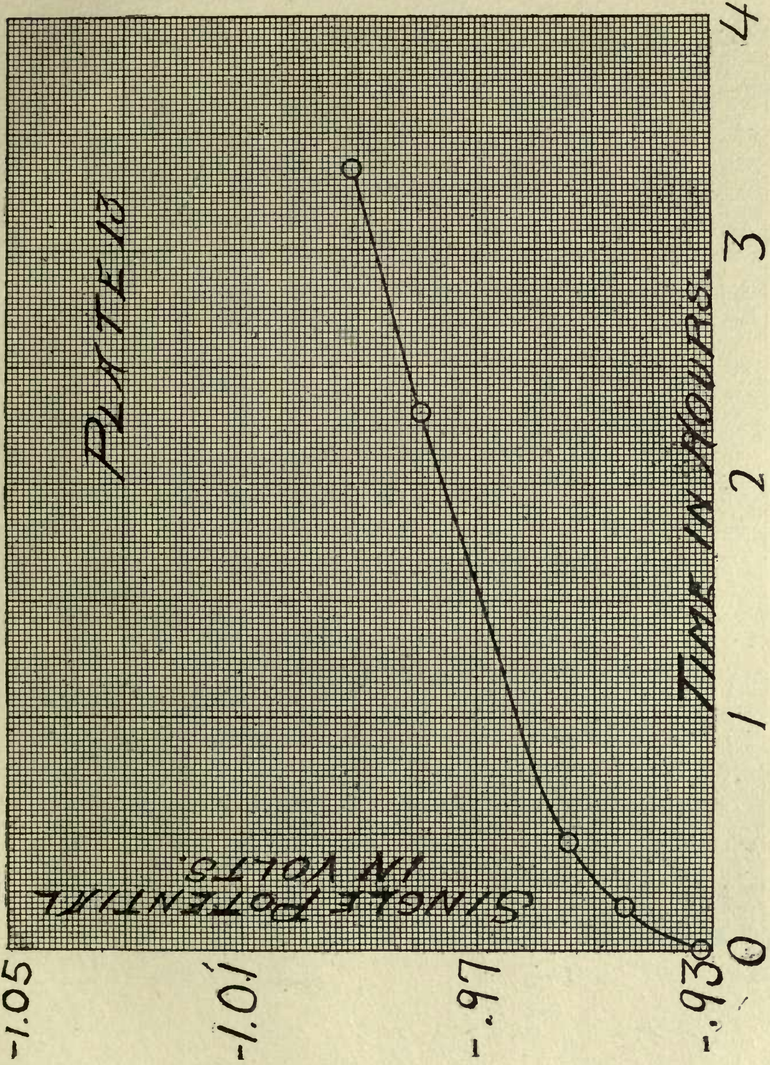


PLATE 13
TIME IN HOURS.
0
1
2
3
4
SINGLE POTENTIAL IN VOLTS.
-1.05
-1.01
-.97
-.93

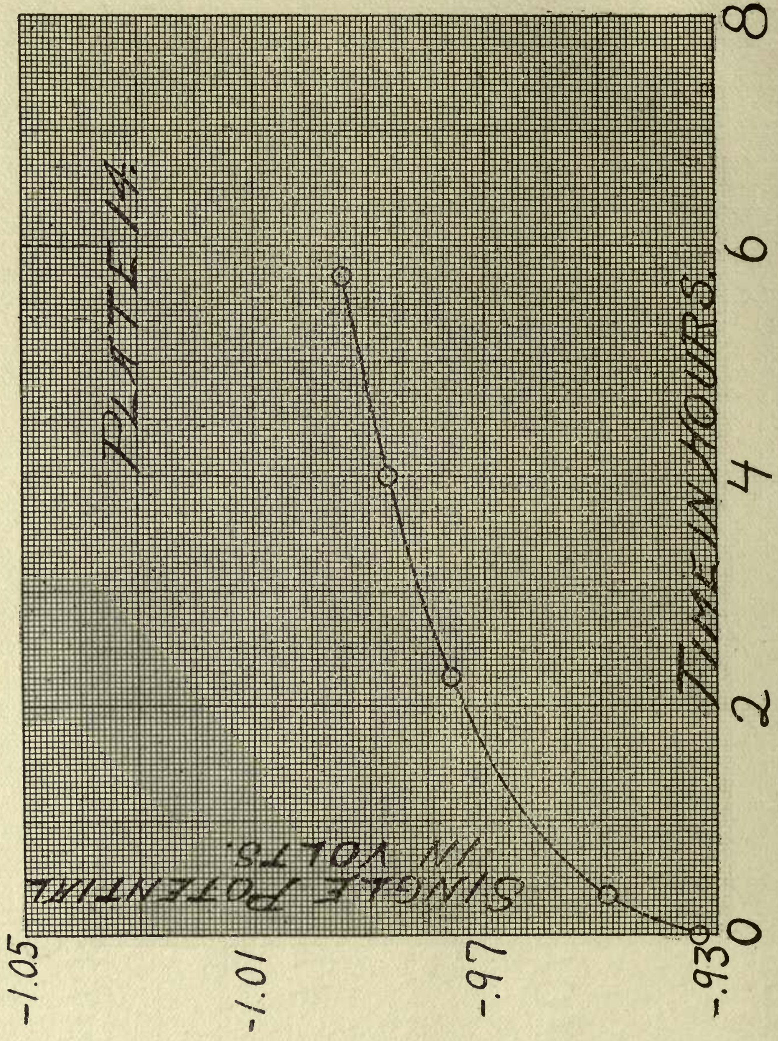


PLATE 14.
TIME IN HOURS
0
2
4
6
8
SINGLE POTENTIAL IN VOLTS.
-1.05
-1.01
-.97
-.93

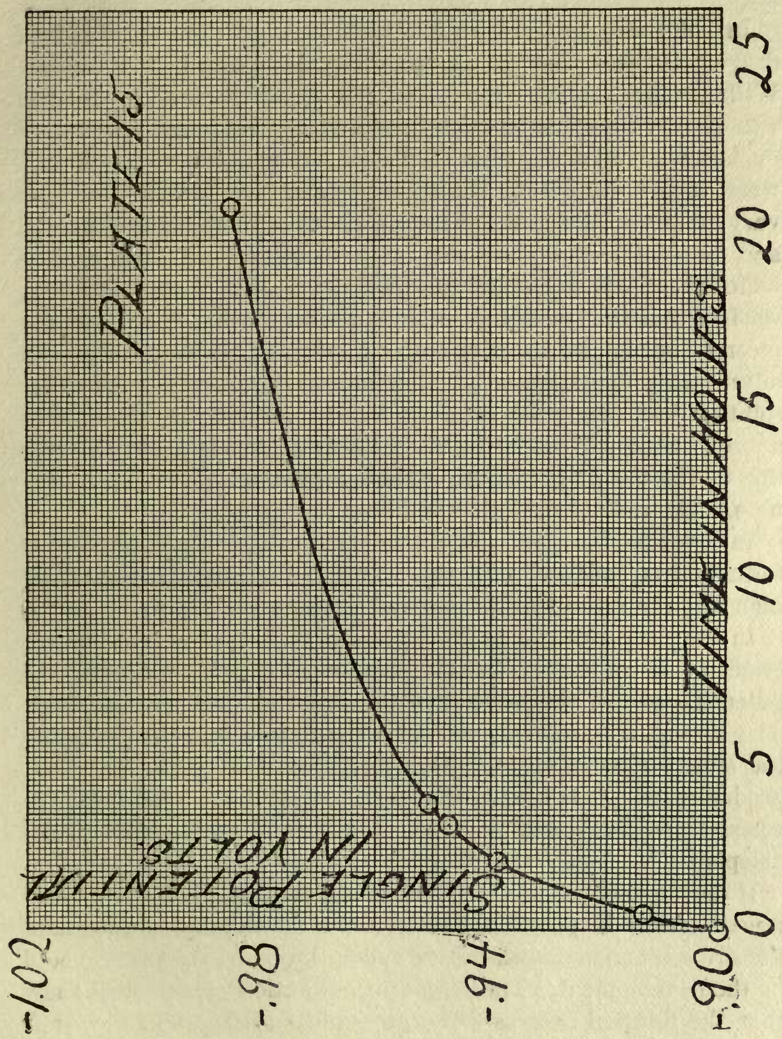


PLATE 15
SINGLE POTENTIAL IN VOLTS
-1.02
-.98
-.94
-.90
TIME IN HOURS
0
5
10
15
20
25

practically the same but the addition of larger amounts of metol seemed to lower the potential while increasing the hydrochinon did not have much effect upon it.

In solutions Nos. 16 to 22, inclusive, solutions of standard developers were made up according to prescribed formulae. With amidol, dianol, edinol, and eikonogen the initial potential was almost identical in each case and the rate and amount of oxidation about the same. This fact becomes very significant when it is noticed that the other constituents of the developer vary greatly in their concentration, and that in the case of amidol and dianol the carbonate was omitted entirely. In the case of metol the single potential was higher, but this is due mainly to the fact that the amount of sulphite was larger than that generally recommended. By referring to Nos. 11 and 12 it is seen that this affects the potential greatly. The rate of oxidation for the metol solution was about the same as for the others. In the case of adurol, solution No. 22, the potential is again high, but this was due to the use of potassium carbonate instead of sodium carbonate. The rate of oxidation is, however, the same.

In solution No. 17 a hydrochinon lantern slide developing formula was followed. In this solution the potential was very high but the rate of oxidation was comparatively slow.

In solutions Nos. 23 to 28, inclusive, the effect of dilution was studied. It was found that the greater the dilution the lower the potential, and at the same time the faster the rate of oxidation. This is what is to be expected, since the more dilute the developer the slower the action and, therefore, the smaller the potential producing it. It is known that sulphite solutions keep better in concentrated form and the same should (and does) apply to developers.

If development is an electro-chemical process, then the greater the difference in potential between the developing solution and the silver bromide and the altered silver bromide, the faster would be the development. The data on the dilution experiments show that the dilution decreases the potential and from practice it is known that it decreases the rate of development. This would indicate that the greater the potential the faster the rate of development. It also seems that the potential of the standard developing solutions, *i.e.*, those recommended for general use, are all practically the same, which fact indicates that there is a certain definite potential which should exist in development in order to produce the best results. This is known to be true in practice, for it is not practical to use either too strong a developing solution as it produces fog, nor too weak a one as it gives too much contrast. The increased contrast produced by using a dilute developer is probably partially due to the fact that the potential is not great enough to decompose the silver bromide except in those parts which have been very strongly attacked by the light.

For each brand of plate there is a certain developing solution which works better than solutions of different concentration. From the work here reported it would seem that it is largely a question of getting a solution of the proper potential for that particular plate.

Of course the numerical values of the single potential between platinum black and the various developing solutions do not afford direct data as to the potential existing in the electrolytic cell in operation during the process of development, *i.e.*, the altered silver bromide and the developer, but since the platinum electrode suffers no change the values which would be obtained under the ideal conditions would differ only in magnitude. These differences in the single potential of different developers are due to the different constituents of the developer. That they are not due to one constituent alone can be seen by inspecting Tables 16, 18, 19 and 20. Thus it must be that the differences are due to all of the constituents in part.

The following conclusions are drawn from the work described in this paper:

1. In developers it is the sodium sulphite which is oxidized.
2. The greater the potential existing between the altered silver bromide and the developer the more rapid is the development.
3. The more dilute the developer the greater is the oxidation.
4. The potential of the developing solution is not due to any one constituent, but to all working together.
5. For every brand of plate, and every kind of plate, there is probably a certain potential which should be maintained in order to secure the most satisfactory results.

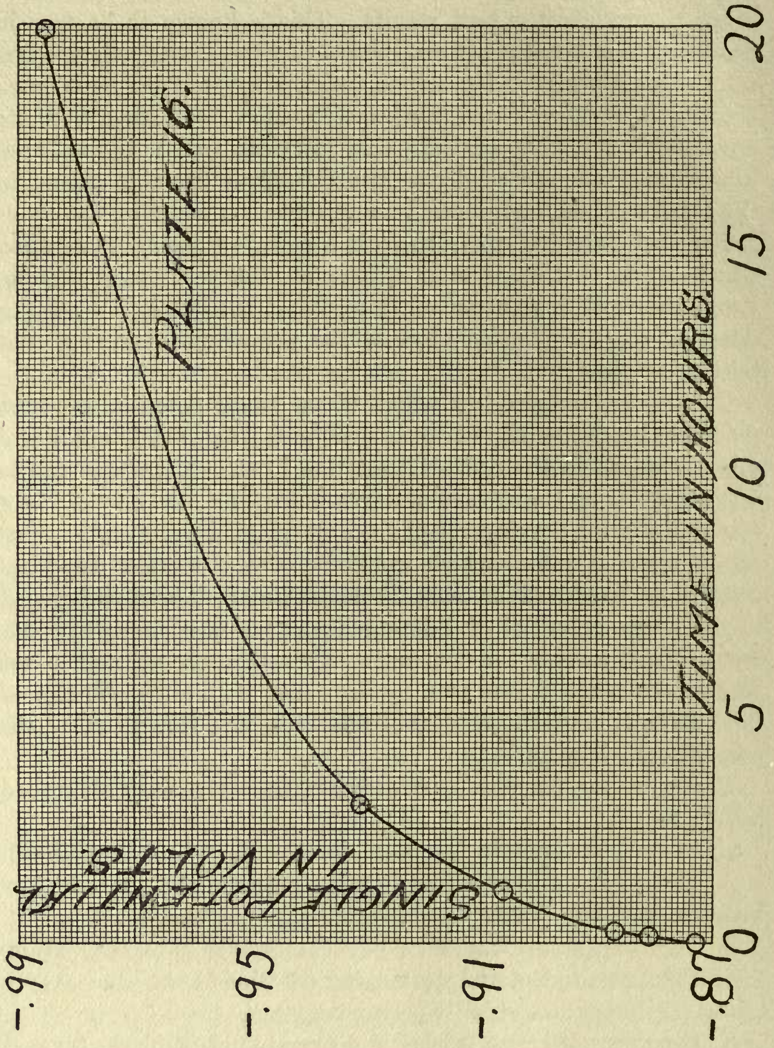


PLATE 16.
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS
0
5
10
15
20
-.87
-.91
-.95
-.99

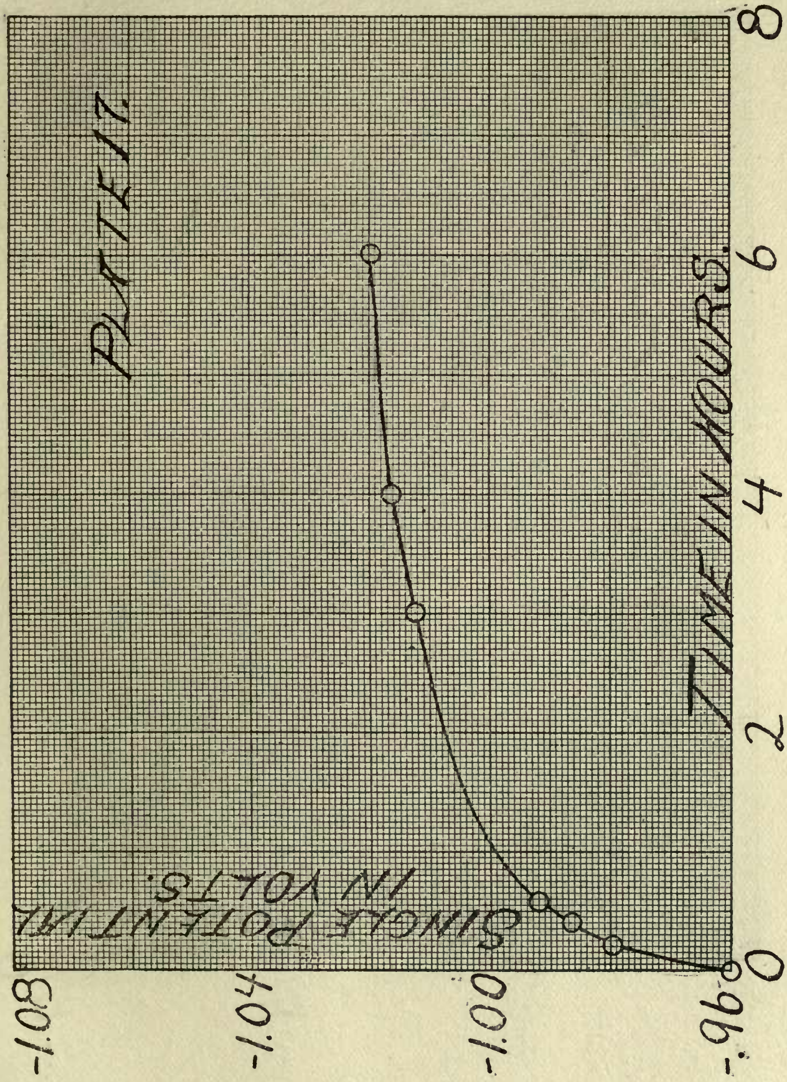


PLATE II.
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS.
0
2
4
6
8
-.96
-1.00
-1.04
-1.08

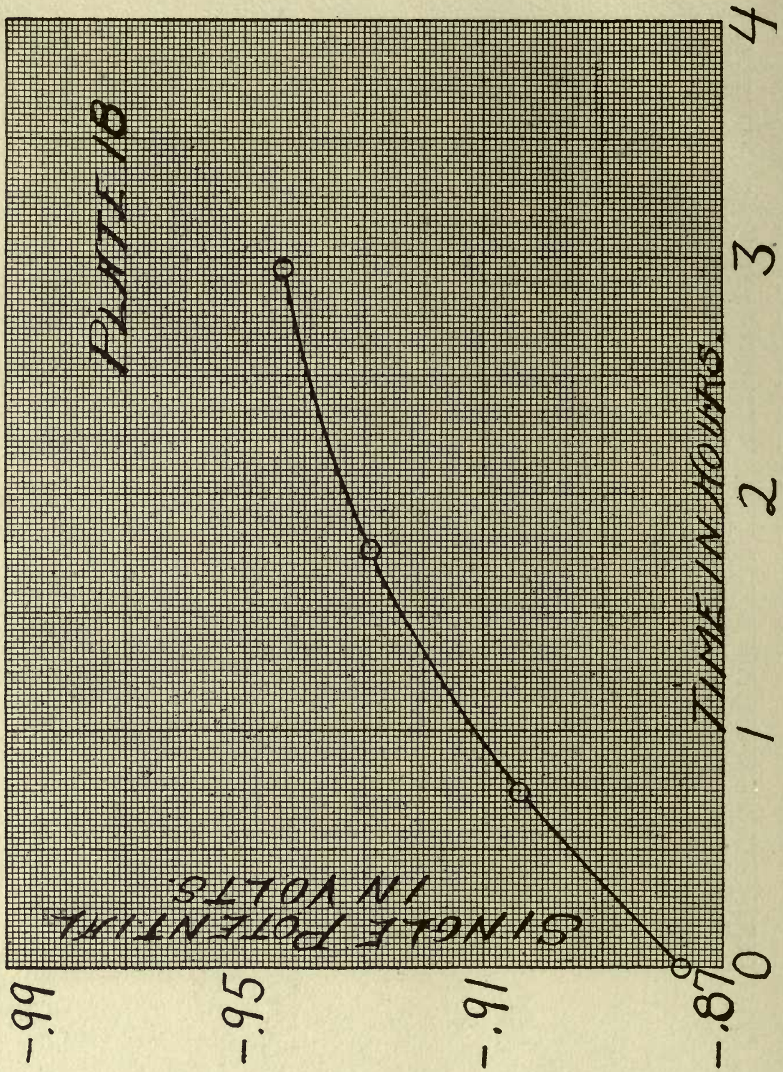


PLATE 18
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS.
0
1
2
3
4
-.87
-.91
-.95
-.99

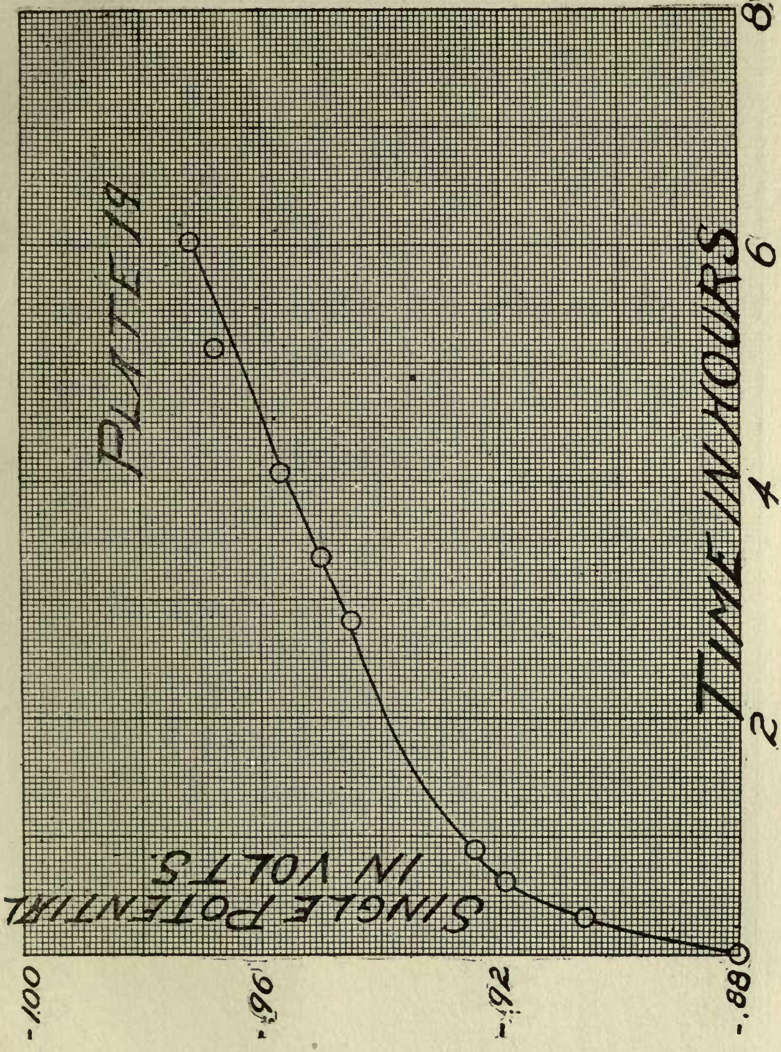


PLATE 19
TIME IN HOURS
2
4
6
8
SINGLE POTENTIAL
IN VOLTS
-1.00
-.96
-.92
-.88

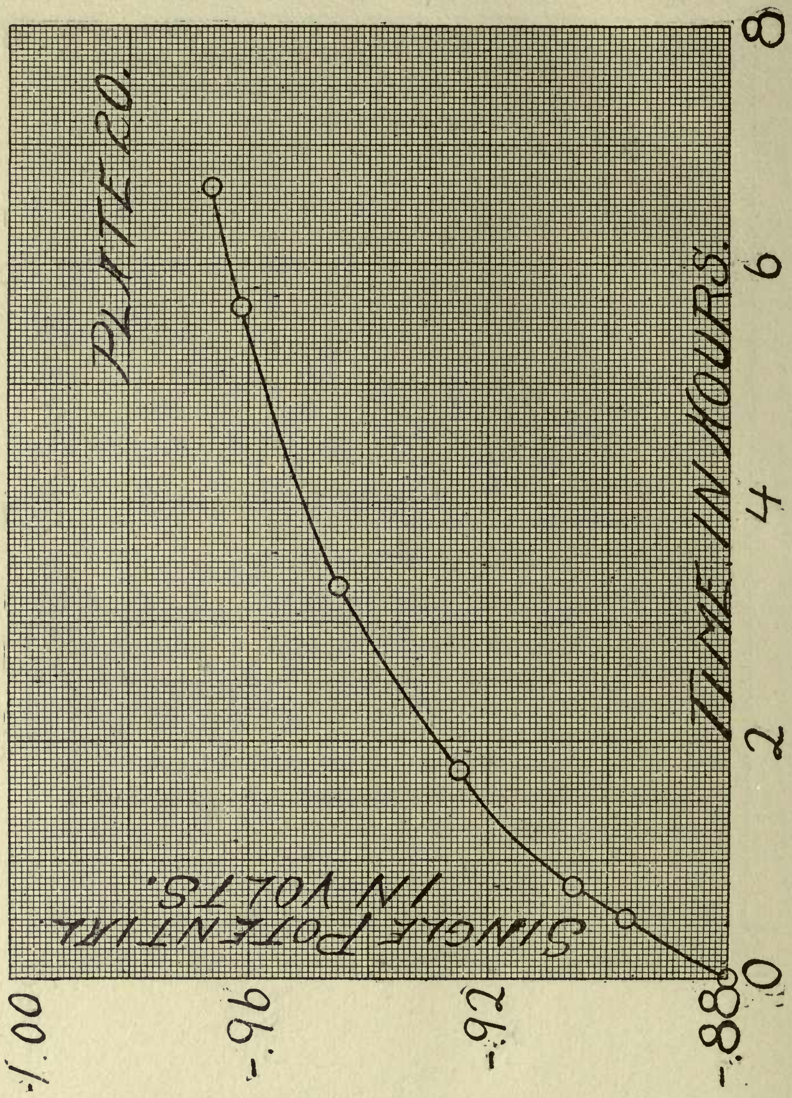


PLATE 20.
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS.
0
2
4
6
8
-.88
-.92
-.96
-1.00

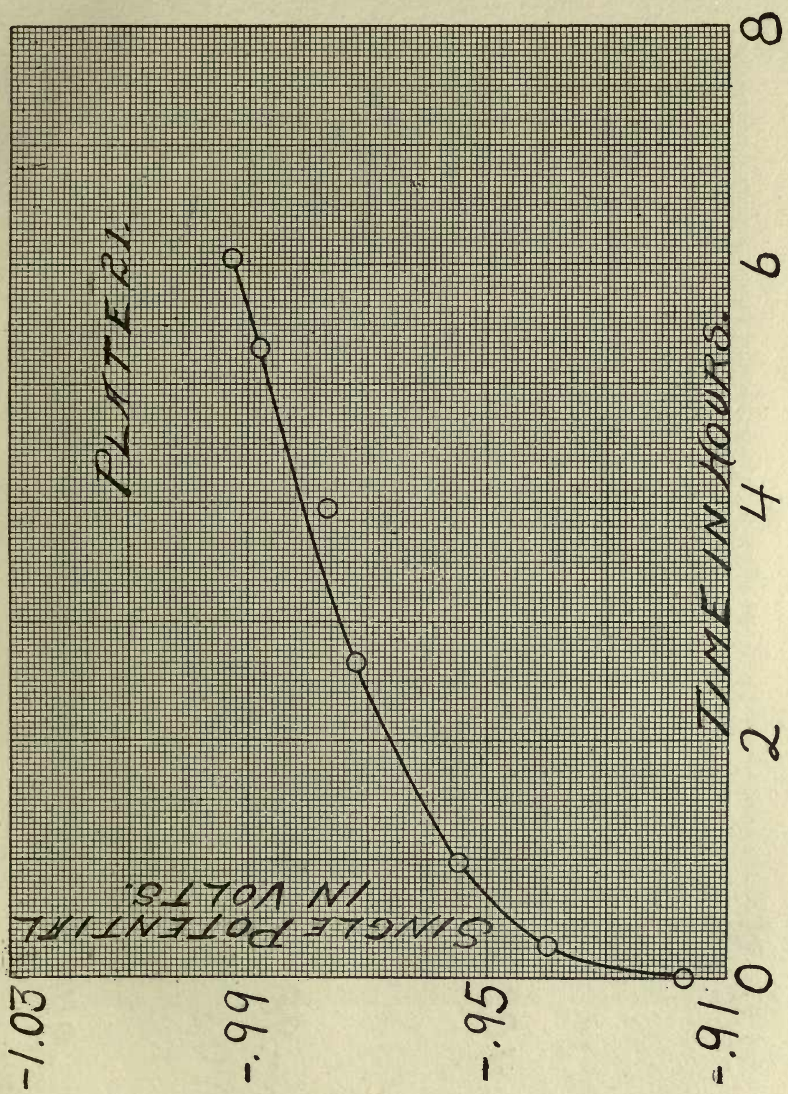


PLATE 21.
TIME IN HOURS.
0
2
4
6
8
SINGLE POTENTIAL IN VOLTS.
-.91
-.95
-.99
-1.03

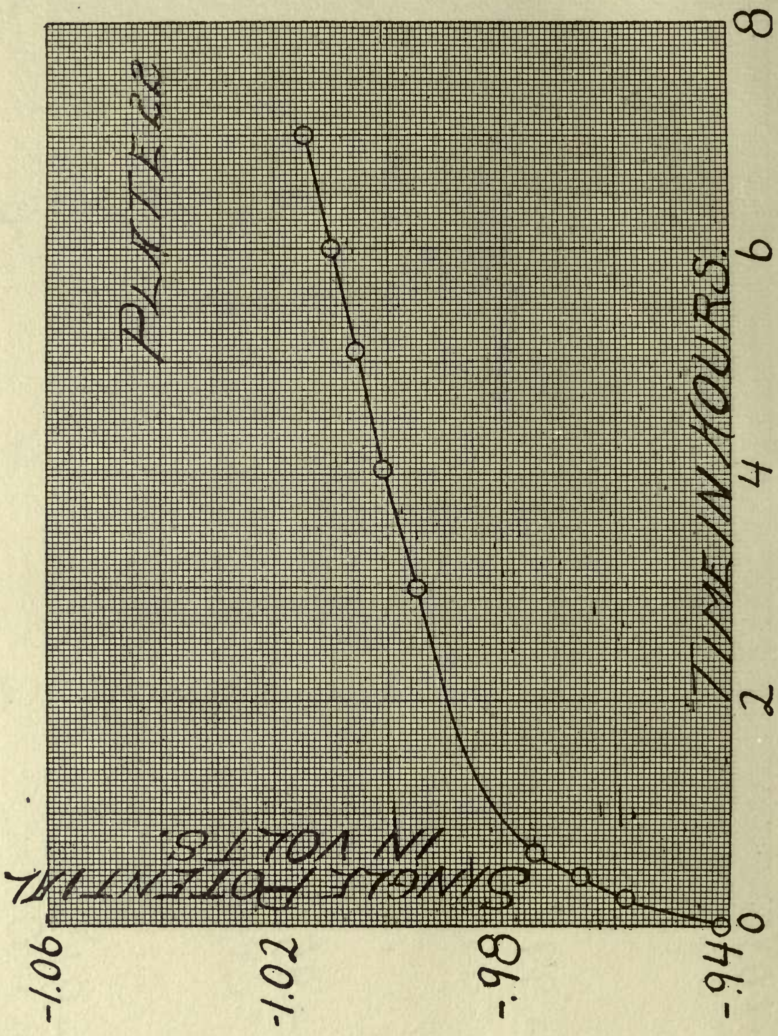


PLATE 22
TIME IN HOURS.
0
2
4
6
8
SINGLE POTENTIAL IN VOLTS.
-1.06
-1.02
-.98
-.94

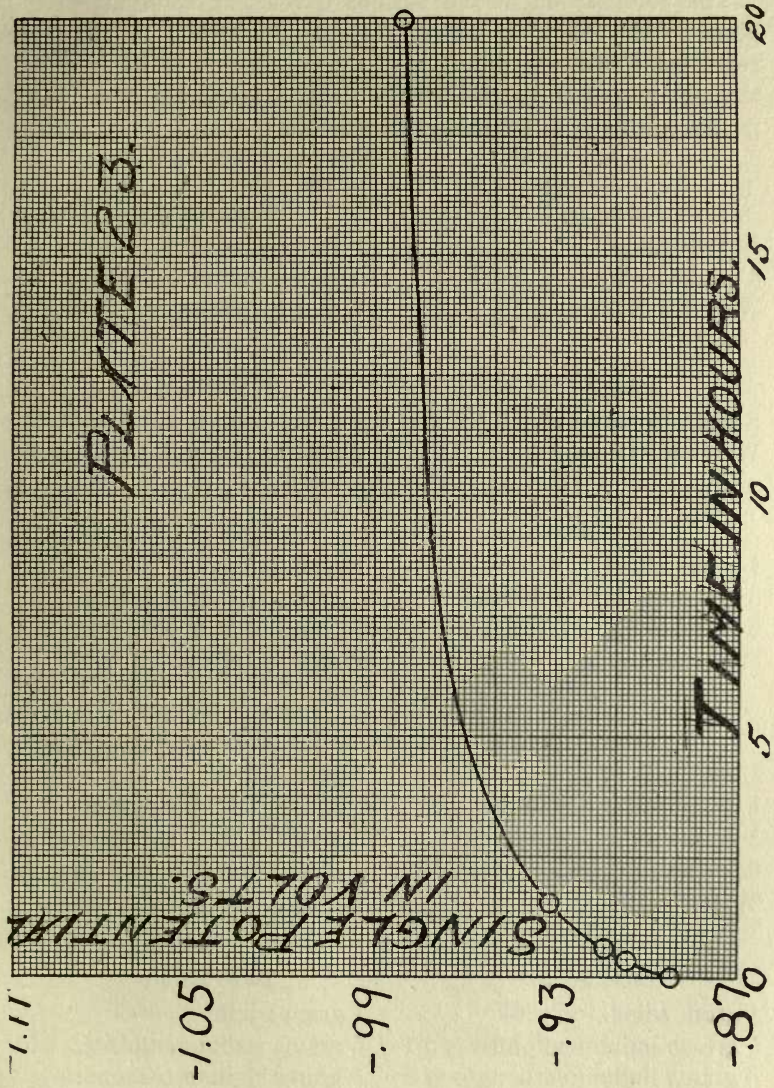


PLATE 23.
TIME IN HOURS.
0
5
10
15
20
SINGLE POTENTIAL IN VOLTS.
-.87
-.93
-.99
-1.05
-1.11

APPENDIX

The composition of the various developing solutions used is given in the following tables. The numbers given on the plates correspond with the numbers of the solutions. It has not been thought necessary to give all the data in tabulated form, as the results will be clear from inspection of the curves.

Table No. 1

1 gram edinol
5 grams sodium carbonate
Water to 100 cc.

Table No. 2

1 gram edinol
5 grams sodium sulphite
Water to 100 cc.

Table No. 3

5 grams sodium sulphite
Water to 100 cc.

Table No. 4

5 grams sodium sulphite
Water to 100 cc.

Table No. 5

1 gram edinol
3 grams sodium sulphite
6 grams sodium carbonate
Water to 100 cc.

Table No. 6

1 gram edinol
5 grams sodium sulphite
5 grams sodium carbonate
Water to 100 cc.

Table No. 7

1 gram edinol
5 grams sodium sulphite
5 grams sodium carbonate
0.5 grams potassium bromide
Water to 100 cc.

Table No. 8

1 gram edinol
5 grams sodium sulphite
5 grams sodium carbonate
1 gram potassium bromide
Water to 100 cc.

Table No. 9

1 gram edinol
5 grams sodium sulphite
5 grams sodium carbonate
0.85 grams sodium bromide
Water to 100 cc.

Table No. 10

1 gram edinol
5 grams sodium sulphite
5 grams sodium carbonate
0.8 grams ammonium bromide
Water to 100 cc.

Table No. 11

0.75 grams metol
2 grams sodium sulphite
5 grams sodium carbonate
Water to 100 cc.

Table No. 12

0.75 grams metol
5 grams sodium sulphite
2 grams sodium carbonate
Water to 100 cc.

Table No. 13

0.5 grams metol
0.5 grams hydrochinon
3 grams sodium sulphite
3 grams sodium carbonate
Water to 100 cc.

Table No. 14

0.5 grams metol
1.5 grams hydrochinon
3 grams sodium sulphite
3 grams sodium carbonate
Water to 100 cc.

Table No. 15

1.5 grams metol
0.5 grams hydrochinon
3 grams sodium sulphite
3 grams sodium carbonate
Water to 100 cc.

Table No. 16

0.7 grams amidol
3.3 grams sodium sulphite
Water to 100 cc.

Table No. 17

1 gram hydrochinon
2 grams sodium sulphite
6 grams sodium carbonate
Water to 100 cc.

Table No. 18

0.5 grams dianol
3 grams sodium sulphite
Water to 100 cc.

Table No. 19

1 gram edinol
5 grams sodium sulphite
5 grams sodium carbonate
Water to 100 cc.

Table No. 20

0.75 grams eikonogen
3 grams sodium sulphite
4 grams sodium carbonate
Water to 100 cc.

Table No. 21

0.75 grams metol
7 grams sodium sulphite
5 grams sodium carbonate
Water to 100 cc.

Table No. 22

1.6 grams dianol
6 grams sodium sulphite
10 grams potassium carbonate
Water to 100 cc.

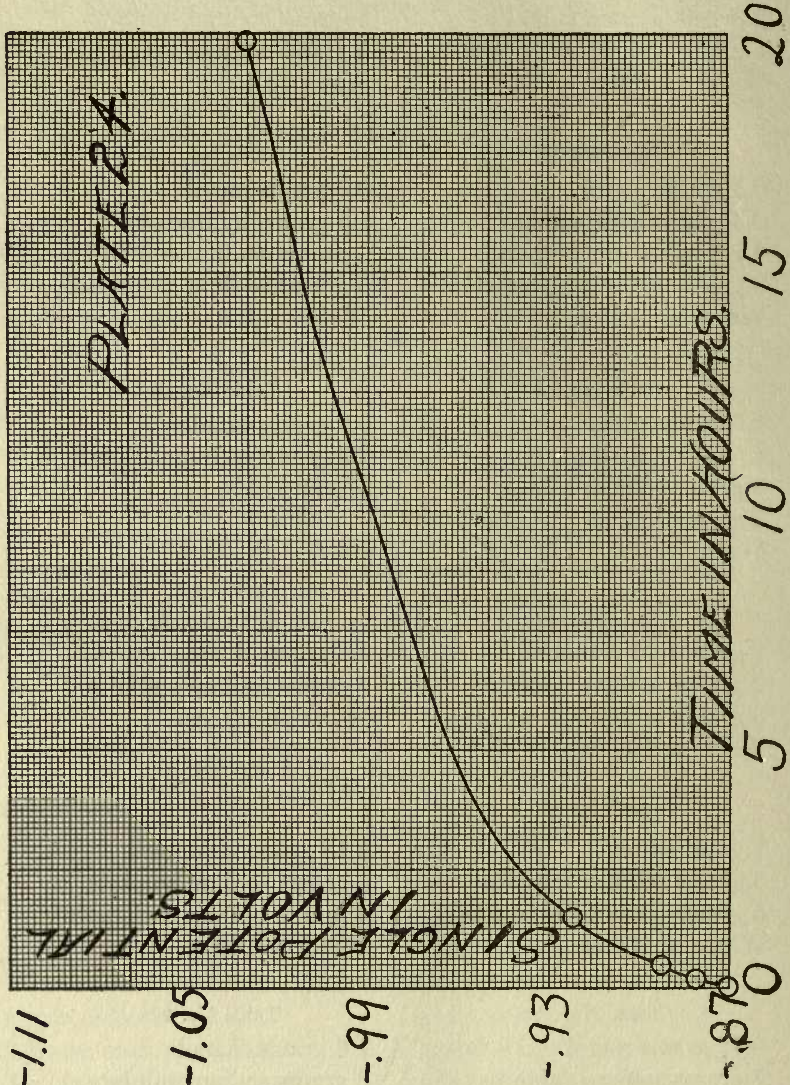


PLATE 24.
TIME IN HOURS.
0
5
10
15
20
SINGLE POTENTIAL IN VOLTS.
-1.11
-1.05
-.99
-.93
-.87

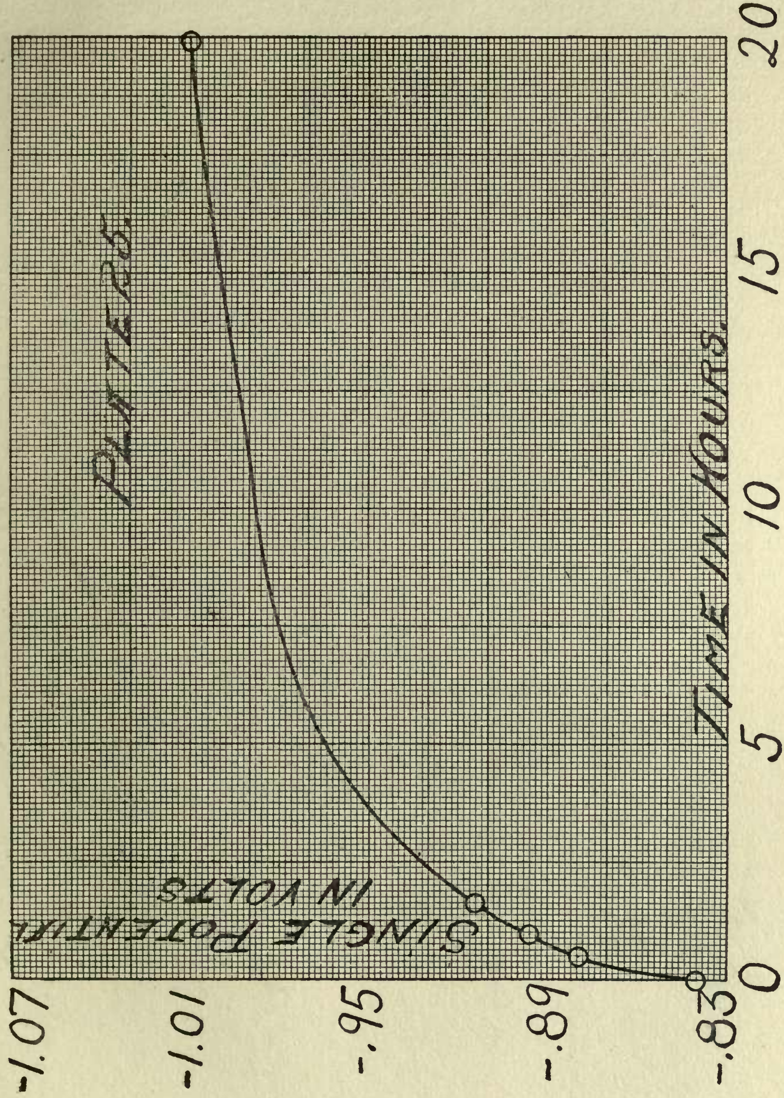


PLATE 25.
SINGLE POTENTIAL IN VOLTS
TIME IN HOURS.
0
5
10
15
20
-.83
-.89
-.95
-1.01
-1.07

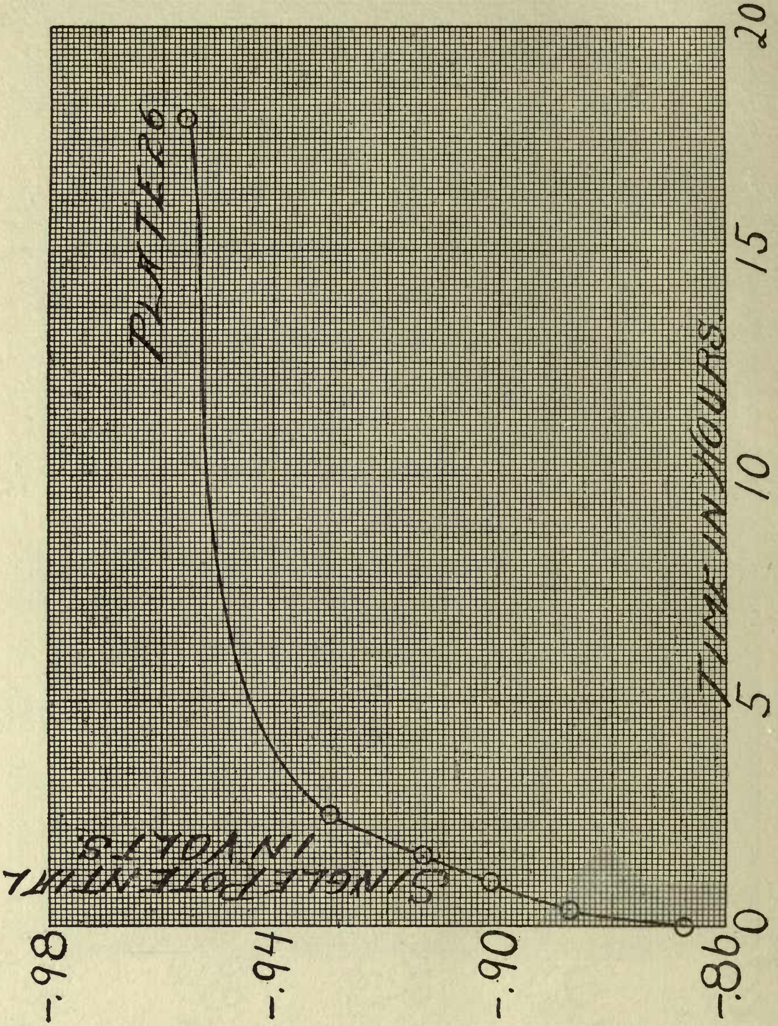


PLATE 26
TIME IN HOURS.
SINGLE POTENTIAL IN VOLTS.
0
5
10
15
20
-.98
-.94
-.90
-.86

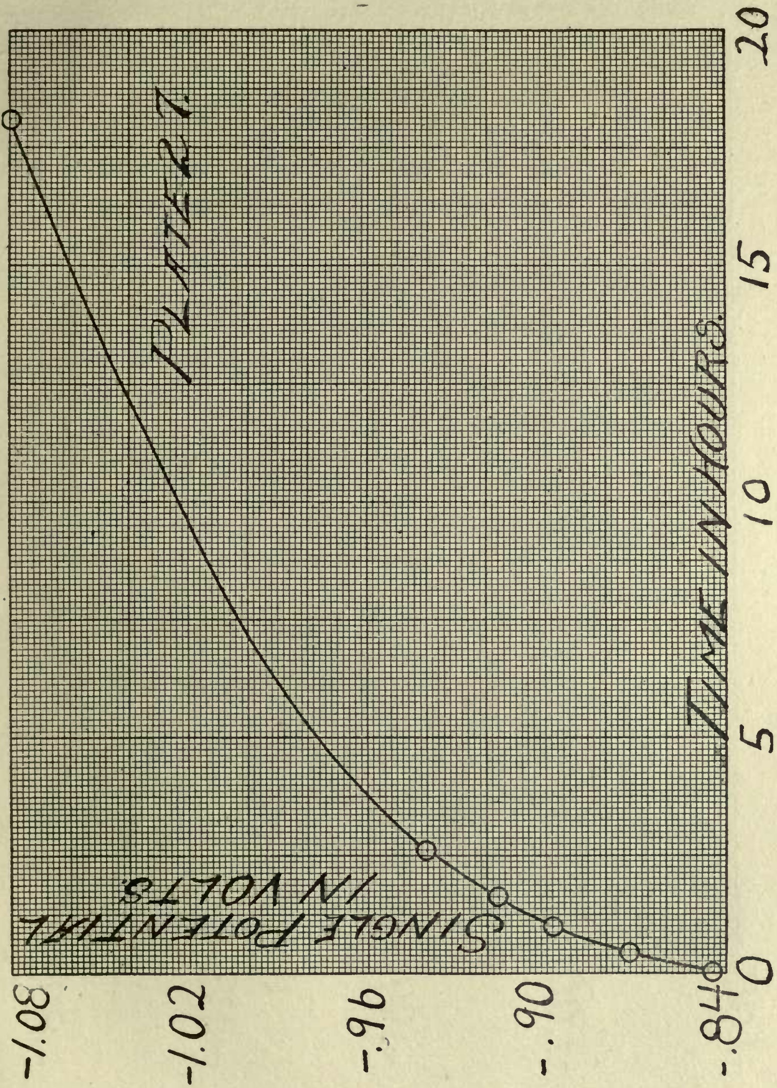


PLATE 27
TIME IN HOURS
0
5
10
15
20
SINGLE POTENTIAL IN VOLTS
-1.08
-1.02
-.96
-.90
-.84

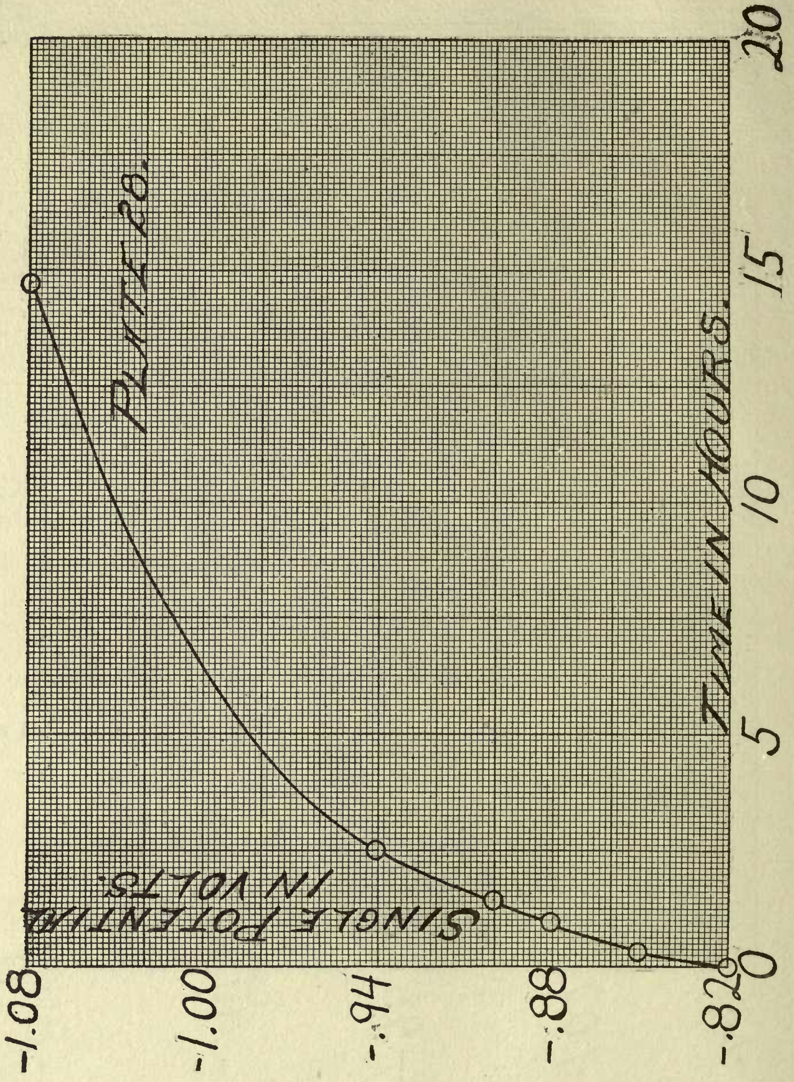


PLATE 28.
TIME IN HOURS.
0
5
10
15
20
SINGLE POTENTIAL IN VOLTS.
-1.08
-1.00
-.94
-.88
-.82

Table No. 23

1 gram edinol
7 grams sodium sulphite
2.5 grams sodium carbonate
Water to 100 cc.

Table No. 24

0.5 grams edinol
3.5 grams sodium sulphite
1.25 grams sodium carbonate
Water to 100 cc.

Table No. 25

0.25 grams edinol
1.75 grams sodium sulphite
0.62 grams sodium carbonate
Water to 100 cc.

Table No. 26

0.5 grams edinol
2.5 grams sodium sulphite
2.5 grams sodium carbonate
Water to 100 cc.

Table No. 27

0.25 grams edinol
1.25 grams sodium sulphite
1.25 grams sodium carbonate
Water to 100 cc.

Table No. 28

0.1 grams edinol
0.5 grams sodium sulphite
0.5 grams sodium carbonate
Water to 100 cc.

A NOTE ON THE ROLE PLAYED BY THE CARBONATE IN PHOTOGRAPHIC DEVELOPMENT

By J. Howard Mathews and Floyd E. Barmeier
University of Wisconsin, Madison, Wis.

The statement is commonly made that the function of the carbonate in a photographic developer is to open the pores of the gelatin so as to provide readier access for the developer to the altered silver halide grains.

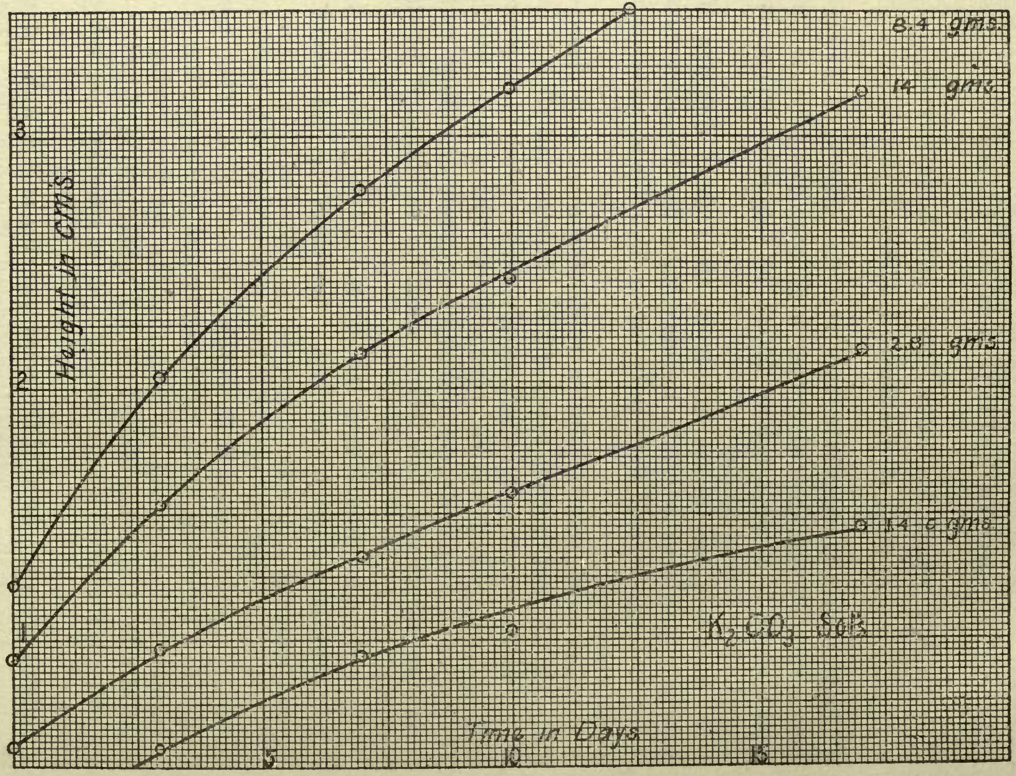
No record of any measurements on the rate of diffusion of carbonate solutions into gelatin having come under the observation of the writers it seemed to us to be highly desirable to make such measurements.

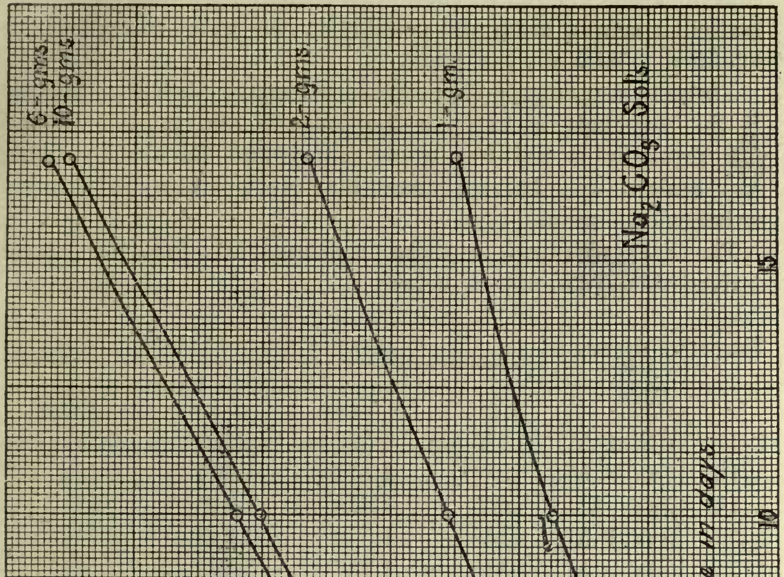
A rather thick gelatin solution containing a trace of phenolphthalein was cast in glass tubes of ¼ in. diameter and allowed to set. The tubes were then cut off sharply so as to produce a square edge and the gelatin was cut square across with a sharp knife. The tubes so prepared were placed in solutions of sodium and potassium carbonates, care being taken to insure their being immersed to the same depth.

The carbonate diffused into the gelatin and produced a pink color having a very sharp boundary. The rise of the pink column in the tubes was accurately measured by a good cathetometer.

It was found that the rate of diffusion increased with the concentration up to a certain limit and then fell off again. This may be due to a hardening action of the carbonate on the gelatin. It is curious, and significant, to note that the solution having the greatest rate of diffusion is one having a concentration of carbonate which is the same as is customarily used in a normal developing solution.

Judging from the form of the accompanying curves which give the behavior of the solutions investigated, it seems likely that there is a certain strength of carbonate solution which would diffuse more rapidly than any other, and that in all probability this would be the concentration most desirable in a developer.


8.4 gms
14 gms
2.8 gms
1.4 c gms
K_2CO_3 Sols
Height in cms
Time in Days
1
2
3
5
10
15


6-gms
10-gms
2-gms
1-gm
Na_2CO_3 Sols
Time in days
15
10
5
Height in cms
3
2
1

Lack of time has prevented our making further determinations along this line. It seems likely that this optimum value for the concentration of the carbonate solution would depend on the particular gelatin used, and possibly on the water content of the solidified gelatin on the plate.

These measurements support the statement that the function of the carbonate is to open the pores of the gelatin—though this probably is not the whole story—and the accompanying curves show why the carbonate may vary within certain, yet rather wide, limits.

The data obtained in these measurements, and the curves derived therefrom, appear below:

Time at which readings were taken		Height of Colored Column			
		Amount of Na_2CO_3 in 100 cc. =			
		1 gm.	2 gm.	6 gm.	10 gm.
3/13	2:30 P.M.	0.520 cm.	0.579 cm.	0.970 cm.	0.932 cm.
3/16	11:00 A.M.	.834	1.118	1.664	1.582
3/18	12:00 M.	1.002	1.344	1.940	1.924
3/20	2:00 P.M.	1.168	1.542	2.242	2.216
3/23	11:00 A.M.	1.346	1.764	2.590	2.556
3/30	11:00 A.M.	1.742	2.332	3.248	3.314
4/12	10:00 A.M.	2.222	3.064	4.262	4.267
		Amount of K_2CO_3 in 100 cc. =			
		1.4 gm.	2.8 gm.	8.4 gm.	14.0 gm.
3/13	2:30 P.M.	0.342	0.582	1.220	0.906
3/16	11:00 A.M.	.582	.976	2.048	1.558
3/18	12:00 M.	.800	1.224	2.430	1.846
3/20	2:00 P.M.	.948	1.360	2.790	2.130
3/23	11:00 A.M.	1.044	1.598	3.236	2.436
3/30	11:00 A.M.	1.478	2.124	4.048	3.180
4/12	10:00 A.M.		2.700	5.184	4.098

THE PRODUCTION OF PHOTOCHEMICALLY ACTIVE RAYS IN ORDINARY CHEMICAL REACTIONS

BY J. HOWARD MATHEWS AND LEON H. DEWEY
University of Wisconsin, Madison, Wisconsin

From time to time for a number of years announcements have appeared stating the discovery of new "rays" having their origin in ordinary chemical reactions. In the attempt to prove the existence of such rays a great number of experiments have been made. Many reactions which were thought to have been productive of such rays have been proven to be ordinary chemical reactions, the gaseous products of which produced the supposed photochemical phenomena.

The latest addition to the literature on this subject appears in the form of an article by Matuschek and Ueming[1] in the Chemiker Zeitung. A brief résumé of their article is as follows:

A beaker containing zinc and hydrochloric acid was placed on a photographic plate in a light-tight case, a tin-foil star being interposed between the beaker and plate. After several hours of "exposure" a distinct image of the star was obtained upon development of the plate. The best results were said to have been found when ribbed (fluted) pieces of zinc were used. Similar results were obtained with hydrochloric and nitric acids acting on copper, tin and lead. The intensity of the new "rays" was found to vary considerably. Copper hydroxide, copper oxide, and potassium hydroxide also gave the photographically active "rays" when dissolved in acids. Other reactions producing the "rays" were: the slaking of lime, the setting of Portland cement, the decomposition of calcium carbide by water and the formation of ammonium amalgam. The reaction producing the strongest "rays" was that between dilute hydrochloric acid and sodium silicate, which gave a distinct image in less than an hour's time.

It was our object to verify, if possible, the results obtained

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[1] Chem. Ztg. *36*, 21 (1912).

by these investigators. A number of the above mentioned reactions—as many as the limited time allowed—were tried.

A light-tight wooden box, 18″x12″x12″ in size, was lined with black paper and the edges padded with black cloth. The plates used were the well known Lumière Sigma plates, these particular plates being chosen because of their extreme sensitiveness. All the manipulations were carried out in a dark room, the plates being developed in darkness.

A plate was placed in the box and a beaker or Erlenmeyer flask containing the metal was placed upon it, a piece of tin-foil being interposed between the beaker (or flask) and the plate. The acid was introduced by means of a separatory funnel which passed out through a light-tight joint in the cover of the box. When a beaker was used the gaseous products of the reaction were not conducted away, but remained in the box where they could come into contact with the plate. When the Erlenmeyer flask was used, however, the gaseous products were conducted away through a delivery tube extending out of the fox, so that by no possibility could the gasses come into contact with the plate.

Experiment I

(a) Action of Dilute (1:3) Hydrochloric Acid on Zinc, in a Beaker.

Here there was no attempt to conduct the gaseous products of the reaction away. Instead of interposing a tin-foil star between beaker and plate, a circular piece of foil, having a circular hole in the center, was used. The diameter of the piece of foil was slightly greater than the diameter of the beaker. After the reaction had been going for an hour or two the plate was removed and developed and an image of the piece of foil appeared, that portion of the plate protected by the foil not being reduced by the developer. However, not only was the plate unaffected beneath the foil but that portion under the hole in the center was also unaffected.

(b) Action of Dilute Hydrochloric Acid on Zinc, in an Erlenmeyer Flask.

In this experiment the same reaction was repeated, but the hydrogen formed in the reaction was conducted away, and upon development the plate showed no sign whatever of reduction.

(c) Plate Protected by Glass.

Experiment (a) was repeated, except that a clean sheet of glass the same size of the plate was placed upon the emulsion and the two plates securely fastened together with strips of adhesive cloth, making it impossible for gasses to come into contact with the emulsion. The beaker was placed upon the plate, with the tin-foil interposed. After twenty-four hours exposure to the reaction the plate showed no signs of reduction upon development.

Experiment II

(a) and (b) of Experiment I were repeated, using dilute nitric instead of hydrochloric acid. In both cases the results obtained were the same as in the previous experiment.

The fact that no reduction was apparent when the gaseous products of the reactions were conducted away led to the following experiment.

Experiment III

In this experiment the action of hydrogen gas on the photographic plate was tried. For this purpose an ordinary hydrogen generator was fitted up and the gas was allowed to impinge upon a photographic plate from a glass tube drawn out to a very fine jet. Upon development the plate was found to be reduced whereever the hydrogen had come into contact with it. Using the hydrogen jet for a pen one can write upon the plate by allowing the gas to impinge upon the plate, the writing remaining invisible until development has taken place.

From these experiments it seems certain that the effects noted by Matuschek and Ueming were due to the gaseous products of the reactions employed. In our first experiment no image of the circular hole in the foil appeared because the pressure of the beaker prevented the gas from reaching this portion of the plate.

Experiment IV

In this experiment the action of dilute hydrochloric acid upon sodium silicate was tried. To 25 cc. of a solution lf sodium silicate contained in a small beaker standing on a plate dilute hydrochloric acid was added. No reduction of the plate could be detected after development, although the reaction was continued for a considerable time.

Experiment V

(a) Water on Calcium Carbide, in a Beaker.

Upon exposure to this reaction for twenty-four hours the plate, where not protected by the foil, was plainly reduced.

(b) Water upon Calcium Carbide, in a Flask.

The same reaction was repeated, but in this case the gaseous products of the reaction were carried away. The plate showed no reduction upon development.

Experiment VI: The Setting of Portland Cement

A sample of ordinary Portland cement was mixed with water and poured into a paste-board ring affixed to a glass plate. This plate was then laid upon a photographic plate in the dark and the cement allowed to set. Although the experiment was continued for forty-eight hours no indication of any reduction could be detected upon development. Had any gas capable of reducing the plate been given off during the process of setting it could not have affected the plate because the emulsion was protected by the glass plate in contact with it.

Experiment VII: The Slaking of Lime

Lime was caused to slake slowly by the frequent addition of small amounts of water. The operation was conducted in a beaker standing upon a photographic plate. After forty-eight hours the plate showed no indication of reduction upon development.

From the results of the foregoing experiments we are led to conclude that the reduction of photographic plates observed by Matuschek and Ueming was due, not to any new kind of "rays," but to the natural gaseous products of the reactions employed. This is substantiated by the fact that there was no reduction in any case where the gaseous products of the reaction were conducted away from the plate, and by the fact that when certain of the gaseous products (viz., hydrogen) were brought into contact with the plate a reduction resulted.

A QUANTITATIVE STUDY OF SOME PHOTOCHEMICAL EFFECTS PRODUCED BY ULTRA-VIOLET LIGHT

By J. Howard Mathews and Leon H. Dewey
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The object of this investigation was to follow, quantitatively, the decomposition and oxidation of various solutions under the action of ultra-violet light. For this purpose solutions of sodium sulphite, potassium permanganate, potassium dichromate, and oxalic acid were used.

A Cooper-Hewitt quartz mercury vapor lamp was used as the source of ultra-violet rays. The lamp was run on a direct current and used three amperes with a potential drop across the terminals of 70 volts. Care was exercised to keep the current strength constant, as the velocity of the reactions studied is so highly dependent upon the strength of the illumination.

The flasks containing the solutions to be worked with were made of transparent quartz, a material which allows the ultra-violet rays to pass freely. They were supported in direct light of the lamp at a distance of 10 cm. Due to the considerable amount of heat generated by the lamp in action, and the heating effect produced by the absorption of the rays, the temperature had to be controlled. This was accomplished by supporting a water-bath immediately under the lamp, connecting it with a water tap and so regulating the flow of water as to keep a constant temperature in the bath. The temperature of the water was kept at about 20°. The quartz flasks were supported on floats in this bath in such a manner that one half of their surface was exposed to the light, the other being exposed to the cooling action of the water. A thermometer kept in the solution indicated its exact temperature. It was found possible to maintain a constant temperature of $25° \pm 1.5°$, which was close enough, as temperature coefficients of photochemical reactions are small.

The solutions used were 0.1 normal. In titrating the weight burette was used. The water from which the solutions were prepared was specially distilled from the city water supply. Potassium permanganate was added to the water before distillation, and the first third of the distillate rejected.

Sodium Sulphite

A liter of 0.1 normal sodium sulphite was divided into two portions of 500 cc. each and placed in glass stoppered litre flasks. One of these was placed in the dark and the other placed in daylight. The solutions were titrated at intervals with a 0.1 normal solution of resublimed iodine. The solution in the light oxidized completely in four days' time, while that portion of the same solution which was kept in the dark for the same period of time was but about half oxidized. From this it was very evident that the oxidation of sulphite solutions is greatly accelerated by light.

Separate experiments in which the containing vessels were entirely filled with the solution showed that in the absence of air the oxidation is but very slight. This slight oxidation is, of course, due to the oxygen contained in the water.

For the study of the effect of ultra-violet light on the oxidation of sodium sulphite solutions, a 0.1 normal solution contained in a quartz flask was placed under the light. It was found that the ultra-violet light has a decidedly accelerating influence on the reaction. The oxidation proceeded about twenty times as rapidly in this light as in the ordinary light of the laboratory.

In order to determine whether there might not be an autoxidation of the sulphite in the ultra-violet light a 0.1 normal solution prepared from boiled water was placed in a quartz flask, care being taken to completely fill the flask. Exposure to the light for six hours produced no appreciable oxidation.

Potassium Permanganate

Solutions of potassium permanganate are usually considered quite stable, although it is known that upon long standing they do change somewhat

A rather strong solution of potassium permanganate was subjected to the action of ultra-violet light for seven hours. It was titrated before and after exposure with a standard solution of

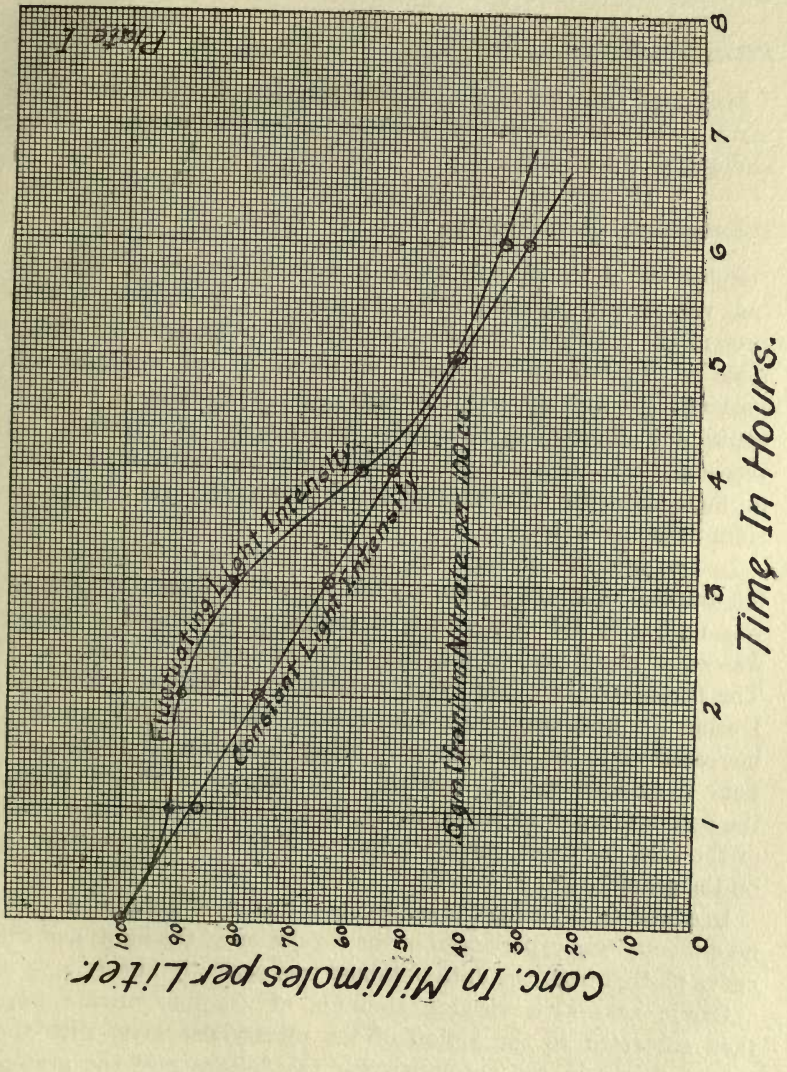
Plate I
Fluctuating Light Intensity
Constant Light Intensity
.6 gm Uranium Nitrate per 100 cc.
Time In Hours.
0
1
2
3
4
5
6
7
8
Conc. In Millimoles per Liter.
100
90
80
70
60
50
40
30
20
10
0

oxalic acid, in presence of sulphuric acid. A slight reduction of the strength of the solution was evident, and a deposit of oxide appeared on the walls of the vessel.

Potassium Bichromate

Six hours' exposure of a 0.1 normal solution of potassium bichromate to the ultra-violet rays produced no change whatever in the strength of the solution.

Decomposition of Oxalic Acid

Solutions of oxalic acid when placed in ultra-violet light are but very slowly decomposed. However, if a uranium salt be present the reaction is greatly accelerated. A series of determinations of the rate of decomposition of oxalic acid solutions with varying amounts of uranium salts, and with salts of uranium containing different acid radicles was made. The nitrate, sulphate and acetate were used. The oxalic acid solutions were 0.1 normal, and were titrated against 0.1 normal solutions of potassium permanganate.

In the first experiment, a solution containing approximately 0.5 gram of uranium nitrate per 100 cc. of 0.1 normal oxalic acid was used. In the first series of titrations considerable trouble was experienced in keeping the intensity of the light constant. This fact accounts for the irregularity shown in the curve (Plate I). During the first two hours the pressure was low, after which it increased while the batteries were being charged until at the third hour the maximum was reached. At the end of the fifth hour the pressure began to fall off again, and the rate of decomposition of the acid decreased correspondingly, all of which is well shown on the graph.

In a later series, using the same concentration of uranium nitrate, no difficulty was experienced in the regulation of the light, and the curve plotted from the data obtained was perfectly linear.

Oxalic acid with varying amounts of uranium nitrate were then subjected to the action of the ultra-violet rays, with the results shown in the accompanying tabulations and the graphs plotted therefrom.

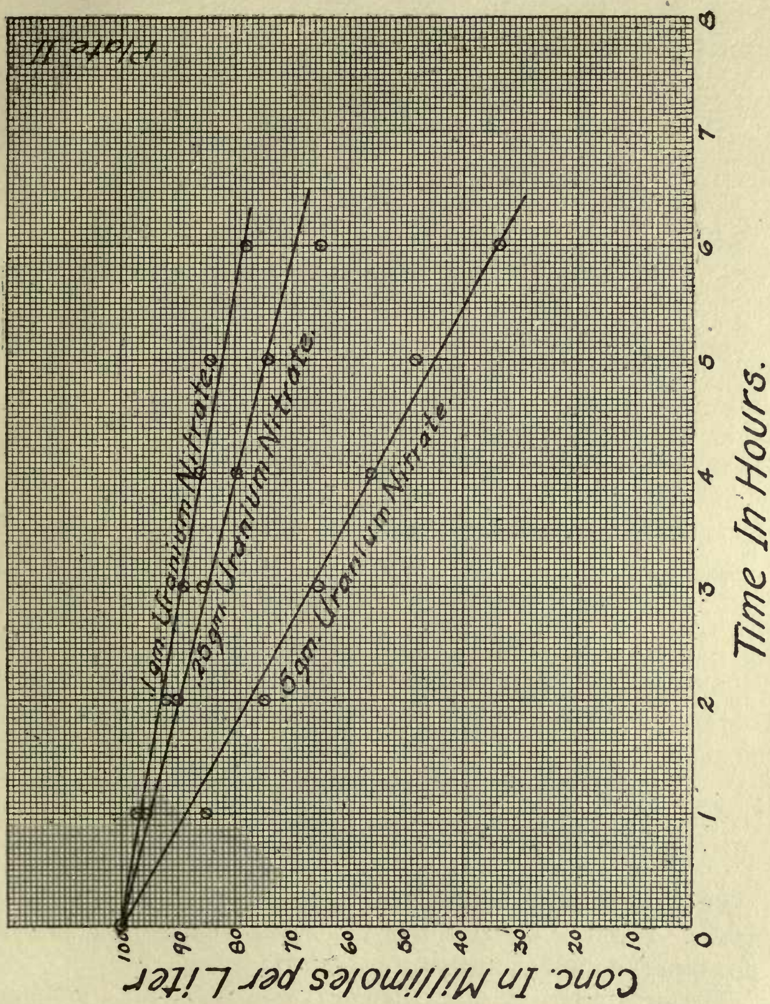
Plate II
.1gm. Uranium Nitrate.
.25gm. Uranium Nitrate.
.5gm. Uranium Nitrate.
Time In Hours.
0
1
2
3
4
5
6
7
8
Conc. In Millimoles per Liter
100
90
80
70
60
50
40
30
20
10
0

Series No. 1. Containing 0.5 gms. uranium nitrate in 100 ccs. of solution

Time of Titration	Millimols of acid present per liter
10:45 a.m.	100.0
11:45 a.m.	85.0
12:45 p.m.	74.9
1:45 p.m.	65.0
2:45 p.m.	56.3
3:45 p.m.	48.5
4:45 p.m.	33.4

Series No. 2. Containing 0.25 gms. uranium nitrate to 100 ccs. of solution

Time of Titration	Millimols of acid present per liter
11:00 a.m.	100.0
12:00 m.	96.0
1:00 p.m.	90.5
2:00 p.m.	85.5
3:00 p.m.	79.4
4:00 p.m.	73.8
5:00 p.m.	65.0

Series No. 3. Containing 0.1 gm. of uranium nitrate in 100 cc. of solution

Time of Titration	Millimols of acid per liter
8:00 a.m.	100.0
9:00 a.m.	97.0
10:00 a.m.	92.0
11:00 a.m.	88.8
12:00 m.	86.5
1:00 p.m.	85.0
2:00 p.m.	77.8

Plate II shows, graphically, the results given in the above tables. It will be observed that the curves are linear, the rate of decomposition being constant.

The next series of determinations were made with uranium sulphate as catalyzer. Since it is the uranium which is the active agent in accelerating the reaction, care was taken to use equimolecular amounts of the different salts.

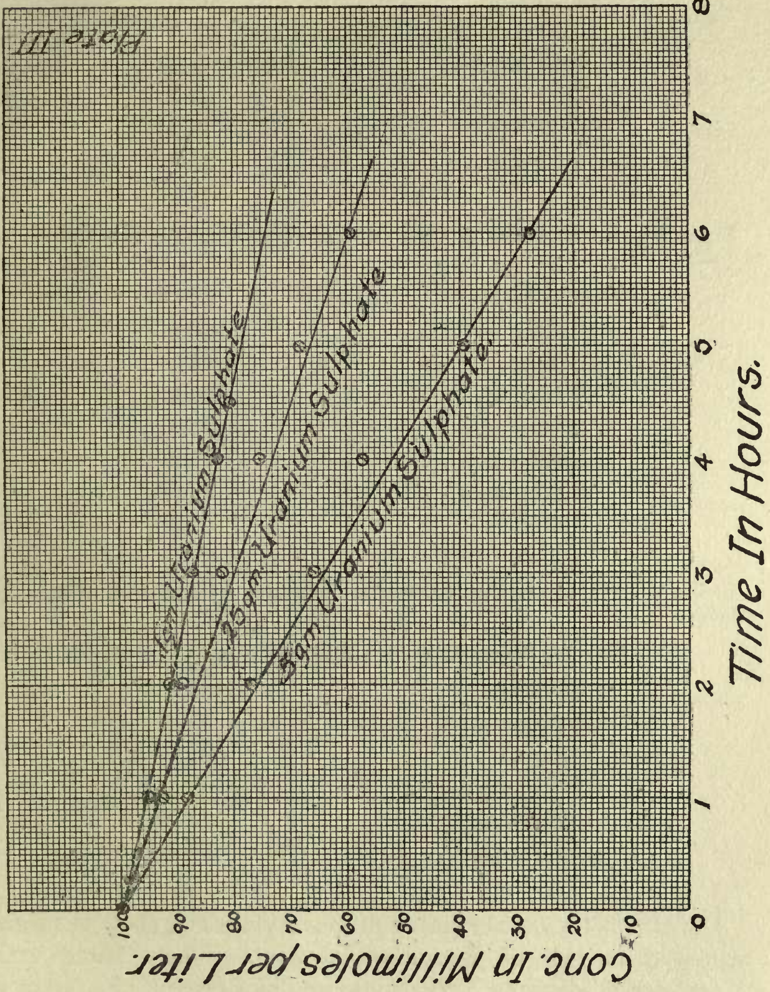
Plate III
15gm Uranium Sulphate
25gm. Uranium Sulphate
5gm Uranium Sulphate.
Time In Hours.
0
1
2
3
4
5
6
7
8
Conc. In Millimoles per Liter.
100
90
80
70
60
50
40
30
20
10
0

Series No. 4. Containing 0.427 gm. uranium sulphate in 100 cc. of solution

Time of Titration	Millimols of acid per liter
10:00 a.m.	100.0
11:50 a.m.	93.0
12:50 p.m.	76.8
1:50 p.m.	65.8
2:50 p.m.	50.7
3:50 p.m.	38.9
4:50 p.m.	27.8

Series No. 5. Containing 0.214 gms. uranium sulphate per 100 cc. of solution.

Time of Titration	Millimols of acid per liter
11:00 a.m.	100.0
12:00 m.	95.0
1:00 p.m.	89.0
2:00 p.m.	81.8
3:00 p.m.	75.2
4:00 p.m.	68.2
5:00 p.m.	59.5

Series No. 6. Containing 0.085 gms. uranium sulphate per 100 cc. of solution.

Time of Titration	Millimols of acid present per liter
8:45 a.m.	100.0
9:45 a.m.	95.2
10:45 a.m.	91.4
11:45 a.m.	87.3
12:45 p.m.	82.5
1:15 p.m.	80.2

The curves for the sulphate solutions, Plate III, show the same regularity in rate of decomposition as previously found with the nitrate of uranium. The more uranium present the faster is the decomposition.

The final series of measurements were made with uranium acetate as the catalyzer, the amounts used being varied as before.

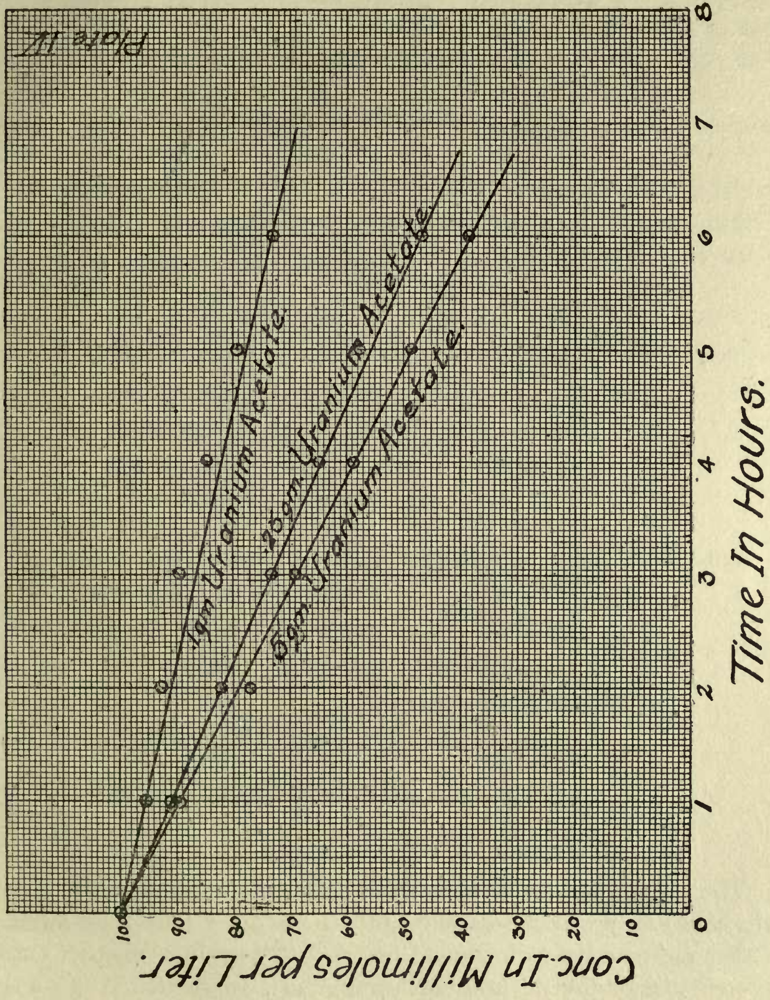
Plate IV
1gm Uranium Acetate.
2.5gm Uranium Acetate.
5gm Uranium Acetate.
0
1
2
3
4
5
6
7
8
Time In Hours.
100
90
80
70
60
50
40
30
20
10
0
Conc. In Millimoles per Liter.

Series No. 7. Containing 0.422 uranium acetate in 100 cc. of solution

Time of Titration	Millimols of acid present per liter
8:15 a.m.	100.0
9:15 a.m.	90.0
10:15 a.m.	77.0
11:15 a.m.	69.8
12:15 p.m.	59.0
1:15 p.m.	48.5
2:15 p.m.	38.9

Series No. 8. Containing 0.084 gm. of uranium acetate in 100 cc. of solution

Time of Titration	Millimols of acid present per liter
11:00 a.m.	100.0
12:00 m.	96.0
1:00 p.m.	93.0
2:00 p.m.	89.8
3:00 p.m.	84.9
4:00 p.m.	78.5
5:00 p.m.	72.6

Series No. 9. Containing 0.211 gms. of uranium acetate in 100 cc. of solution

Time of Titration	Millimols of acid present per litre
10:45 a.m.	100.0
11:45 a.m.	90.5
12:45 p.m.	81.8
1:45 p.m.	73.0
2:45 p.m.	65.0
3:45 p.m.	57.5
4:45 p.m.	46.8

The decomposition of the oxalic acid with uranium acetate as the catalyzer proceeds regularly, as with the other salts of uranium. Other radio-active salts should be tried to ascertain whether this property is limited to uranium compounds, or whether it is common to those possessing radio-activity, It may be that the rays given off from the uranium throw the molecules into an unstable condition which favors their decomposition by the light-waves.

From the experiments described in this paper it is concluded that:

1. The rate of decomposition of a solution by ultra-violet light is dependent upon the amount of light photochemically absorbed.

2. The rate of decomposition of the oxalic acid solutions in the presence of the catalytic uranium salts varies directly with the amount of uranium salt used.

3. The salts potassium permanganate and potassium bichromate are very stable toward ultra-violet light.

4. Sodium sulphite solutions do not oxidize (autoxidation) when air is kept away from them, even under the influence of ultra-violet light, but the oxidation in air is greatly accelerated by such light.

5. Possibly other radio-active elements might behave similarly to uranium in its accelerating action on the decomposition of oxalic acid.

A REVIEW OF THE PROGRESS IN THE THEORY OF PHOTOGRAPHY SINCE THE LAST INTERNATIONAL CONGRESS

By J. Howard Mathews and George W. Heise
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The exact nature of the latent image continues to be a topic of much discussion, however but little new light has been thrown on this subject since the last Congress. An excellent résumé of the arguments for and against the various theories so far suggested was presented at the 1910 International Congress of Photography in Brussels by R. Luther.[1] He considers that, although the "pulverization" of silver bromide by light and other agents seems definitely proven, it offers no explanation of a large number of chemical facts which suggest the reduction of the silver halide. No theory so far advanced satisfactorily accounts for all the observed phenomena, yet, in his opinion, the theory that metallic silver is the reaction product seems the more probable. Luther thinks the problem may never be solved, since the passage from chemical combinations to mixtures and absorbed substances is of the most gradual kind. Mees and Wratten[2] have prepared emulsions containing silver acetylide in gelatine, which proved to be ten times as fast as silver chloride paper. No latent image was produced, however. All parts of the plate, exposed or unexposed, develop similarly. The authors see in this an argument against the subhalide theory, since here no sub-salt is possible. That silver nitride, like silver chloride, turns violet in the light, with the evolution of nitrogen and the appearance of metallic silver, was shown by Wöhler.[3] Mercury nitride becomes orange, also showing finely divided metal. The fact that the sensitiveness to rise in temperature and to shock is the same before and after illumination indicates the formation of a metal, not a subnitride.

[1] Phot. Rundschau, *24*, 221 (1910). Brit. Jour. Phot. *57*, 651 (1910).
[2] Brit. Jour. Phot., *55*, 831 (1908).
[3] Oesterr. Chem. Ztg., *14*, 268 (1911).

In their opinion, this constitutes evidence in favor of the theory that the latent image consists of an adsorptive combination of silver chloride and colloidal silver. Trivelli[1] is of the opinion that a series of subhalides containing gradually decreasing proportions of halogens is formed in the photochemical decomposition of the silver halides. From observations of the color changes which take place under different conditions, the color sequence of the successive subhalides has been found to be: green, blue-green, blue, violet, red, orange, yellow. In a later article[2], various facts are enumerated which tend to show that the structure of the silver halide molecule is complicated, and the progressive changes are discussed in the light of Ostwald's law of successive transformations. An interesting controversy on this subject by Trivelli, Idzerda, and Schaum is to be found in Phot. Korr. 1910 ff. Wöhler and Rodewald[3] (cf. Wöhler and Kasarnowski) have taken the position that the assumption that the color of solid halides is due to the presence of subhalides is as probable as that it should be due to particles of metallic silver. In this connection, a number of new subhalides have been prepared, none of them subhalides of silver, however. Experiments made by Lüppo-Cramer[4] on the coloration of silk, wool, cotton and other fibrous substances upon boiling with solutions of colloidal silver, confirm the view that photohalides consist of normal halide with adsorbed silver, the color depending upon the size of the adsorbed colloidal particles. K. Sichling[5], by means of measurements of potential and electrical determinations of solubility, shows that the photochlorides are single phase systems,—solid solutions of amorphous silver; he furthermore shows that silver chloride and colloidal silver possess continuous miscibility. Baur[6], discussing Sichling's work, concludes from the analogy of $H_2O + SO_3$ that the possible combinations are but one,—Ag_2Cl, which is in dissociation equilibrium with its components Ag and AgCl. In this connection, Reinders[7] has prepared the crystallized photohalides colored with

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[1] Proc. K. Akad. wetensch. Amst., *11*, 730 (1909).
[2] Zeit. wiss. Phot., *9*, 185 (1911).
[3] Zeit. anorg. Chem., *61*, 54 (1909).
[4] Zeit. chem. Ind. Kolloide, *8*, 42 (1911). Phot. Korr., *48*, 188 (1911).
[5] Zeit. phys. Chem., *77*, 1 (1911). Phot. Korr., *48*, 33 (1911).
[6] Zeit. phys. Chem., *77*, 58 (1911).
[7] Zeit. phys. Chem., *77*, 213 (1911).

colloidal silver. He further discusses[1] the subhalide as opposed to the silver adsorption theory and concludes that the evidence would indicate that photohalides are normal silver salts, colored by a small amount of colloidal silver. The different properties of photohalides and of the latent image must then depend on the number, form and distribution of these colloidal particles in solid silver halide. Since the same sequence of colors:—yellow, orange, red, violet, blue,—observed in the reduction of gold or silver solutions and ending with the coagulation of the metal,—may also be observed in the illumination of photohalides, it is probable that the difference in the colors of photohalides must be ascribed to a difference in the size of the silver particles.

The "pulverization" theory is confirmed by Lüppo-Cramer[2] by an interesting experiment, in which a silver mirror is exposed to iodine vapor, whereupon it becomes coated with a film of silver iodide. The plate thus prepared is exposed to light for ten to fifteen minutes. When brushed with cotton, silver iodide as a fine powder is removed only from the exposed portions. F. F. Renwick's[3] "explosion" theory, based on an observation of Scheffer that the silver bromide grain on exposure violently throws off a part of its substance, rupturing the surrounding gelatine, assumes that the silver bromide grains are enclosed in a tangled mesh work of gelatine and can be attacked only—either through the remaining minute channels or by diffusion of the substance through the gelatine skeleton. The explosion of the silver bromide grain disrupts the gelatine, forming channels of relatively large size, giving far better access for the developer to the silver bromide grains. A ripened emulsion is therefore one in which the crystallization occurring during cooking has reached the limit of stable equilibrium, the grain being then in an "explosive" state.

It has been pointed out by Lüppo-Cramer[4] that the substance of the negative is not merely a silver precipitate in gelatine. There is a brown residue left on the treatment of a negative with persulphate (or other oxidizing agents like nitric acid or chromic acid) consisting of adsorption combinations of the silver gel

[1] Zeit. phys. Chem., *77*, 356 (1911).
[2] Phot. Korr., *47*, 226 (1910).
[3] Brit. Jour. Phot., *58*, 48 (1911).
[4] Phot. Rundschau, *24*, 226 (1910).

with parts of the fixing material or of its decomposition products. Homolka[1] had previously assumed that the composition of the image varies with the developer and explained the different colors of the image as being due to combinations of the silver with oxidation products of the developer. Lumière and Seyewitz show that the reduction product is not pure silver,[2] but that it encloses a large quanity of iodine and a small quantity of sulphur in silver bromide-iodide-gelatine plates; with silver bromide-gelatine plates, sulphur only is occluded, but in larger amounts. With potassium cyanide fixing bath, with silver bromide or silver bromide-iodide plates, the reduction product contains no bromine, traces only of iodine, and a small quantity of a dark silver subcyanide (?). The results explain to a certain extent why silver images are not wholly acted upon by many substances known to be solvents for metallic silver, e.g., cerium per-salts and potassium permanganate.

C. Jones[3] has shown that the color of the developed image depends upon the size of the individual granules and that there is no relation between the color of the particles and their distance apart.

Trivelli[4] has attempted to explain why silver chloride printing out paper shows greater decomposition in daylight than the more sensitive silver bromide gelatine plate. He concludes that the relatively small size of the silver chloride particles accounts for the greater activity, and shows mathematically that the blackening should be more intense for small grains.

Lüppo-Cramer[5] has published an interesting set of photomicrographs showing the increase in the size of grain in the process of ripening. Liesegang[6] has pointed out that the ripening of solidified silver chloride gelatine emulsions can be explained only by an intermediate state of solution of the particles of silver chloride, since there is no possibility here of an agglomeration of the individual particles. Trivelli[7] concludes that the ripening process

[1] Jahrb. Phot., (1907).
[2] Bull. Soc. franç phot., (3), *3* No. 1, (1912).
[3] Jour. Soc. Chem. Ind., *30*, 712 (1911).
[4] Zeit. wiss. Phot., *9*, 142 (1910).
[5] Phot. Rundschau, *25*, 176 (1911).
[6] Zeit. phys. Chem., *75*, 374 (1911).
[7] Zeit. wiss. Phot., *8*, 17 (1908).

begins with the conversion of the colloidal silver halide into a crystalloid, which is deposited in the form of very small diamond-shaped crystals. When this conversion is about complete, the continuation of the ripening process consists in the growth of some of the larger particles at the expense of the smaller. Stenger[1] has made the interesting observation that in the ripening of panchromatic plates by heating, the sensitiveness for green and orange increases relatively more than that for blue, a fact which is of considerable practical importance.

An extensive review of the literature of optical sensitizers occurs in the Jahrbuch für Photographie for 1909, to which reference only can be made.

By the use of suitably prepared emulsions, Lüppo-Cramer[2] has produced first and second reversal in red light. The apparently antagonistic effect of red light on solarization is considered to be itself a normal solarization effect. Trivelli has taken exception to Lüppo-Cramer's conclusions. For discussion, cf. Phot. Korr. 1910, 1911, 1912.

The interesting observation has been made by Moncetz[3] that a previously solarized plate exposed to the spectrum, shows, on development, a darkening in the infra-red. This impression is completely effaced by a very short exposure to ordinary light, especially to the blue rays, following the exposure to the spectrum radiation. Similar phenomena were observed in the ultra-violet. The possibility is suggested of using this property of the solarized plate in the photography of the infra-red.

A discussion of the cause of reversal and its remedy, by E. Sanger Shepherd[4] deals with the discovery by Caldwell of the advantages derived from the use of hydrazine, which allows of practically any length of exposure without reversal. These plates have recently appeared on the market.

The comparative reducing power of developers, and means for increasing or reducing contrast in negatives, have been studied by Lumière and Seyewitz.[5] For details, the original must be

[1] Jahrb. Phot., *25*, 50 (1911).

[2] Phot. Korr., *47*, 576 (1910) ff.

[3] Comptes. rendus., *148*, 406 (1909).

[4] Brit. Jour. Phot., *58*, 603 (1911).

[5] Bull. Soc. franç. phot., (2), *25*, 269 (1909). Brit. Jour. Phot., *56*, 162 (1909).

consulted. The same authors point out[1] that the increased contrast produced by potassium bromide is not produced by halides in general, nor by other substances which retard development. This peculiarity of bromine is explained on the supposition of the formation of compounds less easily reduced by the developer than the silver bromide itself. Lüppo-Cramer[2] considers the action of bromides in developers as a colloidal phenomenon. Shepherd[3] takes exception to this view, since the action of bromides in development is a reversible process. Namias[4] observes that the addition of boric acid makes the bath more susceptible to potassium bromide and greatly increases its keeping qualities. Bourgeois[5] has made a detailed study of the effect of sodium carbonate in various developers.

The chemistry of the photographic plate and the analogy between photographic and electro chemical reactions have been very fully discussed in a series of articles by Bancroft[6]. The various theories and observations which have appeared from time to time are here brought together and analyzed. An electrochemical theory of development has also been advanced by Desalme[7]. In the case of ordinary alkaline development, this theory assumes the dissociation of the alkaline electrolyte, the reaction of the sodium ions with the insolated silver bromide to form silver and sodium bromide, and the saturation of the hydroxyl ions by the reducing agent which is therefore simply a depolarizer. The ordinary developer then consists essentially of an electrolyte supplying O and OH ions, a depolarizer (quinonizable organic substance) capable of absorbing those ions, sodium sulphite (when needed to prevent stain), and, in certain cases, a substance (restrainer) impeding the action of the electrolytic process more or less.

The explanation by Russel and others of the action of organic substances on plates in the dark as being due to the formation of

[1] Rev. gen. chim., *13*, 128 (1910).
[2] Zeit. chem. Ind. Kolloide, *4*, 92 (1909).
[3] Zeit. chem. Ind. Kolloide, *5*, 43 (1909).
[4] Atelier Phot., *16*, 120 (1909).
[5] Brit. Jour. Phot., *58*, 650 (1911).
[6] Jour. Phys. Chem., *14*, 12 (1910).
[7] Bull. Soc. franç. phot., (3), *2*, 75 (1911).

hydrogen peroxide, has been studied and extended by Brooks[1]. Benzo-peracid, acetyl peroxide and benzoyl acetyl peroxide each affected the plate, giving a developable impression. Saeland[2], studying the supposed photographic action of metals, points out that the metals, with respect to their activity, arrange themselves in the order of the electrochemical series. Since at the temperature of liquid air, or if, immediately after polishing, the metal is placed in a vacuum, dry air or dry hydrogen, there is no action, the supposed photographic effect of the metals is due to hydrogen peroxide and not to "metal" rays.

Interesting photographs by means of ultra-violet and infra-red rays have been made by R. W. Wood[3] and possible useful applications have been indicated. For the infra-red, the emulsion of Ritz[4] has been shown to be specially applicable.

In color photography, the most important recent advances have been the introduction of the Ives[5] and Tripak[6] processes, the new Krayn[7] color screen, the Dufay[8] dioptichrome plate and the improved Uto color paper of J. H. Smith.[9] For details, the literature referred to must be consulted.

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[1] Phillip. Jour. Sci., (A), *4*, 451 (1909).

[2] Ann. Physik, *26*, 899 (1908).

[3] Brit. Jour. Phot., *57*, 817 (1910).

[4] Arch. Sci. phys. nat. (4), *32*, 485 (1911).

[5] Jour. Soc. Chem. Ind., *29*, 542 (1910).

[6] (Blackburn) Brit. Jour. Phot. Supplement, *57*, 41 (1910).

[7] (Blackburn) Brit. Jour. Phot. Supplement, *58*, 67 (1911). (Valenta) Brit. Jour. Phot. Supplement, *57*, 30 (1910). (Scheffer) Brit. Jour. Phot. Supplement, *57*, 89 (1910).

[8] (Corke) Brit. Jour. Phot. Supplement, *57*, 57 (1910).

[9] Brit. Jour. Phot. Supplement, *57*, 34 (1910).

PRELIMINARY STUDIES ON DIRECT PHOTOGRAPHIC POSITIVES

By G. A. Perley and Alan Leighton
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During the experiments on solarization phenomena conducted by one of us[1] the reversal of the negative photographic image by thiocarbamides was considered.

Colonel Waterhouse[2] found that a positive image resulted in place of the normal negative during some experiments made early in July with an eikonogen developer to which a little phenyl-thiocarbamide had been added. He obtained more or less complete positive pictures not only with the phenyl compound, but also with allyl-thiocarbamide. Thiocarbamide yielded still less regular results, while urea failed to give any sort of a reversal.

The results obtained by Colonel Waterhouse left much to be desired in clearness.

After many trials during the first experiments on solarization a more or less satisfactory positive was obtained by adding a small amount of thiocarbamide to a hydroquinone developer. The work was conducted during the warm summer months.

By means of a preliminary immersion of the plates in the thiocarbamide solution, and washing in running water for a short time, fairly consistent positives were obtained for exposures a little below the normal. Such results seemed to warrant a theory of sensitizing action.

As the previous work had not created a really practical method for the production of direct positives, it seemed advisable to clear up the weak points. It was evident that a detailed study of conditions was essential for a clear understanding of the process.

At first a developer of the following composition was made.

Solution A	Solution B
1,000 grams water	1,000 grams water
126 grams Na_2SO_3 (anhyd.)	126 grams Na_2CO_3 (anhyd.)
21 grams hydroquinone	

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[1] Perley: Jour. Phys. Chem. *13*, 630 (1909).
[2] Waterhouse: Proc. Asiatic Soc. of Bengal. Aug. (1890).

The thiocarbamide was made according to the method of Reynolds[1]. Ammonium thiocyanate was heated in a round-bottom flask at a temperature of 140 to 180° C for five hours. The remaining thiocyanate was extracted with cold water. The thiocarbamide was dissolved in hot water, evaporated and recrystallized. A standard solution of 1 gram of thiocarbamide in one liter of water was employed.

In the early spring, work was undertaken to duplicate former results. The developer consisted of 20 cc. of the thiocarbamide solution, 25 cc. of solution A, and 25 cc. of solution B.

A positive of a brownish purple color was obtained on plates exposed under a standard lantern slide plate. In many cases only a partial reversal resulted.

Much time was expended in varying the different constituents of the developer until a fairly satisfactory positive was obtained. These results are of no importance in the light of our recent work and accordingly may be omitted.

Just as the results seemed to be capable of duplication the warm spring days approached. With this balmy weather some sort of a spring ailment afflicted the developer. None of the much prized previous results could be duplicated.

The first explanation was that of depreciation of the thiocarbamide solution. The solution of thiocarbamide was titrated from day to day with standard permanganate, and the solution was found to remain quite stable. Newly prepared solutions failed to eliminate the trouble.

In order to properly ventilate the dark room during the warmer weather it was necessary to open the windows. At this point it became possible to produce positives of fair quality. The solution of our former troubles became clear. The reactions were exceedingly affected by temperature changes.

As the previous data seemed to be worthless in the light of this last fortunate discovery, and as the reactions involved seemed to attain almost a quantitative aspect, a new source of attack was formulated.

Every variable involved was placed under quantitative control. Separate standard solutions of each of the constituents of the developer were made, and all other factors were standardized.

[1] Reynolds: Jour. Chem. Soc. *22*, 1 (1869).

The 5 x 7 camera employed was made by the Eastman Kodak Co. and equipped with a Cooke anastigmat lens, series III f/6.5 made by Bausch & Lomb.

A standard photograph was located 19 inches from the lens of the camera and illuminated by means of a Cooper Hewitt mercury arc lamp whose center was 22 inches above the photograph. All photographs were taken with the widest stop (f/6.5).

The following standard solutions were employed:

Thiocarbamide,	1 gram per liter
Hydroquinone,	21 grams per liter
Na_2CO_3 (anhyd.),	126 grams per liter
Na_2SO_3 (anhyd.),	126 grams per liter

Each of these solutions was measured from a standard burette. A burette stand was located in the dark room in such a manner that the four burettes were compact, yet easily accessible. The water was measured by means of a pipette.

Considering that the source of illumination and actinic value of the light was maintained constant by the above precautions, and that a plate of the same emulsion was employed, we recognized the following variables: time of exposure, temperature of development, time of development, size of plate, amount of thiocarbamide, hydroquinone, soldium carbonate, sodium sulphite and water. A total of nine variables had to be considered before the perfect conditions could be understood.

The plates employed in this work were purchased at different times, but the Seed 26 X plate was always used.

Each one of the constituents was measured into a glass tray and the whole developer was thoroughly mixed before immersing the plate. The developer was used for one experiment and then discarded.

Using the concentrations that had previously given the best results the data of Table I were obtained.

The results of Table I show that only one temperature can be employed for the particular concentration of developer used. The temperature was controlled by inserting the tray of previously cooled developer into a mixture of ice and water maintained at the desired temperature.

TABLE I

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6⅔	8	8° C.	5 m.	0.02	0.273	1.512	0.504	85	Thin negative
2	6⅔	8	10° C.	5 m.	0.02	0.273	1.512	0.504	85	Thin negative
3	6⅔	8	12° C.	5 m.	0.02	0.273	1.512	0.504	85	Best positive
4	6⅔	8	14° C.	5 m.	0.02	0.273	1.512	0.504	85	Fogged positive
5	6⅔	8	16° C.	5 m.	0.02	0.273	1.512	0.504	85	Heavy fog
6	6⅔	8	18° C.	5 m.	0.02	0.273	1.512	0.504	85	Heavy fog

A difference of two degrees centigrade from the best conditions yielded an absolutely worthless plate.

The influence of temperature on this reaction is enormous. This undoubtedly explains the reason for the better success attained previously by a preliminary immersion in running water. During the hot months this served to cool the developer to the essential temperature conditions.

In view of these data all future work was conducted at 12° C. during development.

The results of Table II were obtained by varying the content of thiocarbamide.

TABLE II

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6⅔	8	12° C.	5 m.	0.006	0.273	1.512	0.504	85	Thin neg.
2	6⅔	8	12° C.	5 m.	0.008	0.273	1.512	0.504	85	Partial pos.; high lights neg.
3	6⅔	8	12° C.	5 m.	0.010	0.273	1.512	0.504	85	Partial pos.; high lights neg.
4	6⅔	8	12° C.	5 m.	0.014	0.273	1.512	0.504	85	Fogged pos.
5	6⅔	8	12° C.	5 m.	0.018	0.273	1.512	0.504	85	Heavy fog.
6	6⅔	8	12° C.	5 m.	0.020	0.273	1.512	0.504	85	Best pos.
7	6⅔	8	12° C.	5 m.	0.022	0.273		0.504	85	Thin pos.
8	6⅔	8	12° C.	5 m.	0.024	0.273	1.512	0.504	85	Thin pos.
9	6⅔	8	12° C.	5 m.	0.026	0.273	1.512	0.504	85	Thin pos.
10	6⅔	8	12° C.	5 m.	0.030	0.273	1.512	0.504	85	Thin pos.
11	6⅔	8	12° C.	5 m.	0.032	0.273	1.512	0.504	85	Thin pos.
12	6⅔	8	12° C.	5 m.	0.034	0.273	1.512	0.504	85	Thin pos.
13	6⅔	8	12° C.	5 m.	0.036	0.273	1.512	0.504	85	Thin pos.
14	6⅔	8	12° C.	5 m.	0.040	0.273	1.512	0.504	85	No image

It was evident that at 12° C. the best amount of thiocarbamide was 0.02 grams when used with 85 grams of water, 0.273 grams hydroquinone, 1.512 grams Na_2SO_3, and 0.504 grams Na_2CO_3. This, of course, is not essentially the best developer.

This work brought forth a few interesting points. Only a very small amount of thiocarbamide (0.003 grams per sq. in. of plate surface) is required to produce a positive. Its action with high concentrations is limited by the influence it has as a solvent for the emulsion. In other words, a partial positive results with insufficient thiocarbamide; with a trifle in excess, the reaction is so rapid that a badly fogged plate results; and with still greater amounts, a thin positive with less fog is produced. Above a certain concentration there is only a solvent action.

It was interesting to note that for the lower concentrations a fairly dense reddish-brown deposit was produced, while just beyond the zone of complete fogging (0.02 grams) a brownish purple deposit made up the positive image. The two colors were absolutely different.

The next variable studied was the hydroquinone and the data are given in Table III.

TABLE III

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6¾	8	12° C.	5 m.	0.020	0.126	1.512	0.504	85	Heavy fog
2	6¾	8	12° C.	5 m.	0.020	0.184	1.512	0.504	85	Heavy fog
3	6¾	8	12° C.	5 m.	0.020	0.210	1.512	0.504	85	Heavy fog
4	6¾	8	12° C.	5 m.	0.020	0.252	1.512	0.504	85	Best positive
5	6¾	8	12° C.	5 m.	0.020	0.273	1.512	0.504	85	More dense pos.
6	6¾	8	12° C.	5 m.	0.020	0.294	1.512	0.504	85	Thin positive
7	6¾	8	12° C.	5 m.	0.020	0.336	1.512	0.504	85	Thin positive
8	6¾	8	12° C.	5 m.	0.020	0.357	1.512	0.504	85	Partial neg.
9	6¾	8	12° C.	5 m.	0.020	0.420	1.512	0.504	85	Partial neg.

Table III shows that there is only a comparatively narrow range for the variation of hydroquinone within which good results may be produced.

The action may be best understood by a description of the progress of development. In all cases where a more or less good positive results there first appears a very faint negative on the plate. This develops as a rule after one and a half minutes' immersion; after approximately three minutes, the negative appears to fade into a positive which attains its best contrasts after a total of five minutes' development. The production of a very thin negative seems to be essential to the making of a good positive.

The role of the hydroquinone would seem to be in the production of just the minimum negative to render a positive. Too small amounts would not yield a negative. Hence, there would be a uniform development over the whole surface. This explains the fog. Too large amounts would yield such a dense negative (provided the exposure was sufficient) that it would injure the positive effect.

The very thin negative that seemed essential for the success of the positive creates a thin fog in the high lights of the very best positives.

The amount of sodium carbonate was next varied and the results are given in Table IV.

TABLE IV

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0	85	Blank
2	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.126	85	Very thin neg.
3	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.252	85	Thin negative
4	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.378	85	Best positive
5	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.504	85	Fair positive
6	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.630	85	Very fair pos.
7	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.756	85	Dense pos; high lights neg.
8	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.882	85	Dense pos.; high lights neg.
9	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	1.134	85	Dense pos.; high lights neg.
10	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	1.386	85	Dense partial neg.
11	6⅔	8	12° C	5 m.	0.020	0.252	1.512	1.764	85	Dense partial neg.

Table IV gave results consistent with Table III. With increase of carbonate there is of course an increase in the density of the negative produced per unit time. For excessive amounts of carbonate there would then be a negative masking a positive. The data show one interesting point. There is, off hand, no reason why No. 2 should not have produced the best positive, as the thinnest negative (with no trace of a positive) resulted with this concentration. This result would seem to indicate that a certain amount of carbonate is essential in the production of a positive.

The sodium sulphite was next varied and the results are given in Table V.

TABLE V

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6⅔	8	12° C.	5 m.	0.020	0.252	0	0.378	85	Fogged neg.
2	6⅔	8	12° C.	5 m.	0.020	0.252	0.378	0.378	85	Partial pos.; high light neg.
3	6⅔	8	12° C.	5 m.	0.020	0.252	0.630	0.378	85	Partial pos.; high light neg.
4	6⅔	8	12° C.	5 m.	0.020	0.252	1.008	0.378	85	Fair positive
5	6⅔	8	12° C.	5 m.	0.020	0.252	1.260	0.378	85	More dense pos.
6	6⅔	8	12° C.	5 m.	0.020	0.252	1.386	0.378	85	Dense pos.
7	6⅔	8	12° C.	5 m.	0.020	0.252	1.512	0.378	85	Very dense pos.
8	6⅔	8	12° C.	5 m.	0.020	0.252	1.638	0.378	85	Less dense pos.
9	6⅔	8	12° C.	5 m.	0.020	0.252	1.890	0.378	85	Best positive
10	6⅔	8	12° C.	5 m.	0.020	0.252	2.520	0.378	85	Less dense pos.
11	6⅔	8	12° C.	5 m.	0.020	0.252	2.772	0.378	85	Thin positive

With increase of sulphite there seems to be a maximum in the density of the positive. An increase in concentration of sulphite limits the quality of the positive by a seemingly restraining or solvent action. Since the density of the positive passes through a maximum, it is possible to obtain good results with two different concentrations of sulphite (1.008 grams and 1.890 grams) yet 1.890 grams is the preferable since there is a minimum of darkening in the high lights. The data of No. 1 show that a certain amount of sulphite is necessary for the production of a positive.

The results of Tables I, II, III, IV and V indicated that with an exposure of 8 sec., and a development at 12° C., a developer for a plate with 6⅔ sq. in. of surface area consisting of 0.02 grams thiocarbamide, 0.252 grams hydroquinone, 0.378 grams sodium carbonate, and 1.890 grams sodium sulphite in 85 grams of water was the best. At any rate, consistent results could be obtained.

There are a few criticisms on the positives produced, even under the most ideal conditions. First, each plate has a thin light-brown fog just beneath its surface. The fog does not appear in the slightest by transmitted light, yet upon reflected light it becomes very evident. This only detracts from the appearance of the plate and not from its use. Secondly, the production of a good positive requires a thin, yet distinct, negative. The reduced silver yields in the high lights a very thin fog, while the shadows overmask the negative by the dense positive deposit. The negative is so thin that it does not appear when the plate is used as a lantern slide. Thirdly, the deposits do not have the characteristic black color, but are nearly purple. It is an interesting fact that after fixing and washing, the deposit is of a beautiful sepia tone, while after drying it has a purple hue.

Since the attempt to eliminate the negative by variation of carbonate or hydroquinone was a failure, the time of exposure was varied as a last resort. The results as given in Table VI were obtained.

TABLE VI

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6⅔	2	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Thinly fogged positive
2	6⅔	3	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Thinly fogged positive
3	6⅔	4	12° C.	5 m.	0.02	0.252	1.890	0.378	85	More dense pos.
4	6⅔	5	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Fair positive
5	6⅔	6	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Good positive
6	6⅔	7	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Best positive
7	6⅔	8	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Fair positive
8	6⅔	9	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Fair positive
9	6⅔	10	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Partial neg.
10	6⅔	11	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Nearly all neg.
11	6⅔	13	12° C.	5 m.	0.02	0.252	1.890	0.378	85	Negative

Table VI shows that with too great an exposure the negative develops more rapidly than the positive. For too short exposures there seems to be a uniform surface development. For exposures below six seconds there seems to be an insufficient latent image formed to facilitate the development of a contrasting and dense positive. Thus the data of Table VI are consistent with that of Tables III and IV.

All of the variables had been considered with the exception of the water content. Table I gave indications that there might be a possibility of varying the total concentration of the active agent and thereby to alter the rate of reaction. The results of this work are given in Table VII.

TABLE VII

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	51	Thin negative
2	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	68	Thin negative
3	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	77	Thin negative
4	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	81	Fair positive
5	6¾	6	12° C	5 m.	0.02	0.252	1.890	0.378	85	Best positive
6	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	86.5	Thinner positive
7	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	91	Heavily fogged positive
8	6¾	6	12° C.	5 m.	0.02	0.252	1.890	0.378	101	Fog

Table VII shows that only within a narrow range of total concentration can any sort of a positive result. With a high concentration the latent image is developed the more rapidly and the thiocarbamide exerts a solvent action. With greater dilution, the rate of development of the whole surface becomes uniform with the resultant formation of a fog.

In order to obtain a qualitative idea concerning the effect of plate surface on the process, an exposed plate of the normal size was developed under the best conditions. A second exposed plate was immersed in the same developer. A very badly fogged positive resulted. It thus seemed essential to express the concentration of the developer in plate surface units.

Table VII indicated a method of applying the process at room temperature and accordingly the results of Table VIII were obtained.

TABLE VIII

No.	Size of plate sq. in.	Expos. in sec.	Temp. of dev.	Time of dev.	Gm. thio.	Gm. hydro.	Gm. Na_2SO_3	Gm. Na_2CO_3	Gm. H_2O	Remarks
1	6¾	6	18°	5 m.	0.02	0.252	1.890	0.378	41	Very thin pos.
2	6¾	6	18°	5 m.	0.02	0.252	1.890	0.378	51	Best positive
3	6¾	6	18°	5 m.	0.02	0.252	1.890	0.378	56	Dense and fogged positive
4	6¾	6	18°	5 m.	0.02	0.252	1.890	0.378	61	Fog

The work showed that it is possible to obtain a positive at room temperature, yet the water content must be regulated with great care.

During the work at 12° C. a universal thin haze seemed to appear on all of the plates with the exception of one box. One box of the Seeds 26 X plates gave a very sharp contrasting positive. At the time, this was considered purely a manipulative error. At 18° C. this haze increased slightly in density.

In order to check up the influence of the emulsion on our results a 3¼ x 4 lantern slide plate made by the Imperial Dry Plate Co. was exposed under the same conditions as in the previous work. The developer consisted of 0.0030 grams thiocarbamide, 0.0387 grams hydroquinone, 0.2907 Na_2SO_3, 0.0775 grams Na_2CO_3 and 7.8461 grams H_2O per square inch of plate surface. An exceedingly fine positive resulted, yet with the characteristic minor faults. With a Seed 26 X plate of the same size and developed under the same conditions the thin surface fog was visible. Thus, much depends on the emulsion when perfect results are sought.

This work must be considered as a preliminary study of the process. All indications point to the possibility of producing a direct positive of fine quality.

Experiments are already proceeding with a view of substituting such developing agents as pyrogallol, eikonogen, metol, glycine, pyrocatechin, amidol, rodinal, etc., for the hydroquinone.

The results, to date, indicate that the reducing agent affects the color of the resulting deposit. Eikonogen was found to yield far less fog, no visible negative after fixing, and almost a black deposit. The results on this are very incomplete.

There is also the possibility of substituting allyl thiocarbamide, phenyl thiocarbamide, and in fact, all of the thiocarbamides in place of straight thiocarbamide. The results will be greatly different from our present series. A small amount of work on the allyl thiocarbamide has shown possibilities. In place of the purple deposit consistently obtained by use of thiocarbamide, a most beautiful red deposit results. If it were not for the reddish fog, the present results would yield a plate almost unequalled by hand painting for use as a transparency. The results on this are incomplete.

A later paper on the theory of this process will attempt to clear the problem. Instead of using some thiocarbamide or derivative it should be possible to find some substance that will eliminate the present unpleasant fog.

Other possible sources of attack are in the addition of some type of a restrainer which will restrain the negative and leave the positive unaffected. A small amount of potassium bromide was found to restrain the positive more rapidly than the negative. As yet sodium chloride, citric acid, etc. have not been tried as restrainers.

If the present thin negative and brownish fog formation can be restrained, a perfect plate may be produced at room temperature.

The work is still under investigation.

To summarize:

(1) The work was attempted in order to produce consistently direct positives of good quality.

(2) The production of a positive by the Waterhouse process is most easily influenced by alteration of the conditions governing the reaction.

(3) The variables considered in this preliminary study were: time of exposure, temperature of development, time of development, size of plate, amount of thiocarbamide, amount of hydroquinone, amount of sodium carbonate, amount of sodium sulphite and amount of water. Under the conditions the same emulsion was employed and the source of illumination and actinic value of the light was maintained constant.

(4) The temperature during development must be carefully regulated. Utilizing a given concentration, the temperature cannot be varied more than one degree centigrade.

(5) The quantity of the developer utilized governs the resultant positive. It is best expressed in plate surface units.

(6) By exposing a plate in a camera to an object illuminated by a Cooper Hewitt mercury arc light at a given distance, a positive was obtained after 5 minutes' development in the following solution maintained at 12° C.; 0.0030 grams thiocarbamide, 0.0378 grams hydroquinone, 0.2837 grams Na_2SO_3, 0.0567 grams Na_2CO_3 and 12.7627 grams water per square inch of plate surface.

(7) An excess of any constituent which favors an increase in the development of the latent image yields a partial negative (or a masked positive). An insufficient amount produces uniform development and a resultant fog.

(8) An excess of thiocarbamide acts as a solvent for the emulsion. An insufficiency does not visibly affect the thin negative resulting from normal development.

(9) No single constituent can be omitted from the above developer to obtain good results.

(10) At 12° C. a small quantity of water (high concentration) causes the thiocarbamide to exert its solvent action. A large quantity of water (low concentration) retards the development of the latent image with the production of a fog.

(11) Under the same conditions as in (6) at 18° C. an exceedingly good positive can be obtained on a lantern slide plate with 0.0030 grams thiocarbamide, 0.0387 grams hydroquinone, 0.2907 grams Na_2SO_3, 0.075 grams Na_2CO_3 and 7.8461 grams water per square inch of plate surface.

(12) Work is being conducted on the substitution of eikonogen, metol, pyrogallol, amidol, glycine, rodinal, pyrocatechin, etc., for hydroquinone. Allyl thiocarbamide produces red deposits, while thiocarbamide yields bluish tones. The derivatives are under investigation.

(13) A suitable restrainer for the yellow fog and thin negative would yield great improvements.

(14) The contrast and clearness of the final deposit depend much upon the emulsion on the plate.

(15) The only sources of dissatisfaction with the present positive are: first, the bluish color of the deposit; secondly, the necessity of a preliminary appearance of a thin negative; thirdly, the appearance by reflected light of a yellowish fog.

ABSORPTION SPECTRA IN THE RED AND NEAR INFRA-RED[1]

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The great value of screens transmitting only isolated spectral regions is too well recognized at the present time to require justification. This fact is attested by the numerous investigations which have been carried out on the absorption spectra of both organic and inorganic compounds. While most of the work covers the visible and ultra-violet, much has also been done in the infra-red beyond 1μ. A search in the literature for absorption spectra in the near infra-red has revealed the fact that this region has received but little attention. Considering the very large amount of work which is being carried out at the present time, in phosphorescence and in photography, by means of red-sensitized plates, I have thought it worth while to present a note on the optical behavior of a few substances in the region extending from about 0.55μ to 1.5μ.

The substances to be discussed fall, roughly, under three headings:

1. Colored glasses (ruby, cobalt and chromium).
2. Aqueous solutions of dyes transparent in the deep red.
3. Aqueous solution of neodymium nitrate whose sharp absorption bands serve as convenient marks of reference.

APPARATUS

Light from the Nernst lamp N is first rendered parallel by means of the lens L_1, then passes through the absorption cell C and is focused on the slit S_1 by means of the lens L_2. The mirror spectrometer $M_1PM_2M_3$ projects the spectrum of the source in the plane of the slit S_2, which in turn transmits a monochromatic bundle to

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[1] See Kayser—Handbuch der Spektroscopie, Band III.

Uhler and Wood—Atlas of Absorption Spectra (Carnegie Institution Monograph).

W. W. Coblentz—Investigations in the Infra-Red Spectrum (Carnegie Institution Monograph).

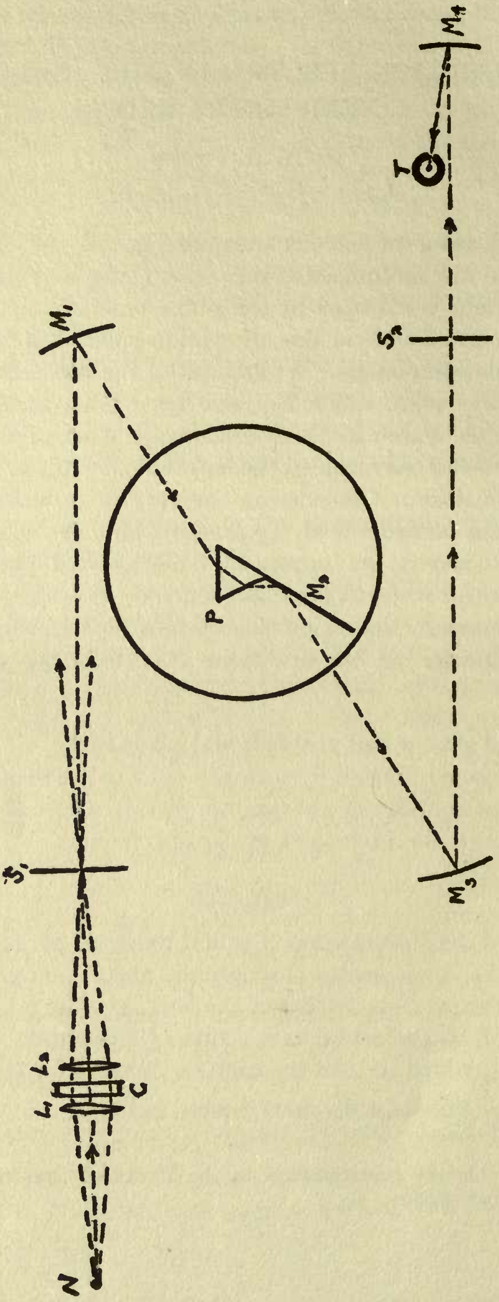


FIG. 1

the mirror M_4. The latter finally focuses the monochromatic slit-image on the blackened junctions of a thermopile T. The lenses and prism in this system are of glass while the mirrors are coated with nickel to avoid tarnishing. The process of coating a glass surface with a highly reflecting layer of nickel is very simple: a thick coating of nickel is first deposited by cathodic disintegration whereupon a wire is soldered to the nickel film and a second layer is deposited electrolytically from the double sulphate of nickel and ammonia. It is only necessary to caution against depositing too thick a layer, since it has a tendency to peel off. The process is completed by polishing with a little rouge on smooth kid leather. Such mirrors as these are but little inferior to fresh silver mirrors. As might be expected, they remain bright for an indefinite period. The thermopile consists of two junctions which are mounted in a highly evacuated capsule, the vacuum being produced and maintained by a charcoal evacuator. Both the thermopile and the evacuator are of new design and have already been described elsewhere.[1] The absorption cell was made of a brass ring (two mm. wide) whose ends were closed by plates of "white" glass. It is essential to avoid the use of glass plates which appear greenish when viewed edge-on, for such plates absorb red and infra-red rays very markedly. In order to eliminate as much as possible the effect of diffusely scattered and reflected radiations of greater wave-length, a layer of water one cm. thick was inserted in front of the slit S_1 as long as measurements were being carried out for wave-lengths less than 1.2μ. Whenever, in the following, absorption spectra of solutions are discussed, it is to be understood that aqueuos solutions are under consideration. Since, in photography, one is interested only in the total amount of radiation passing through the absorbing screen, no attempt has been made to determine the absorbing properties of the dissolved substance by itself. The terms "Percentage transmission" are defined as being the ratio of the intensity of monochromatic radiation when the light passes through the cell, to that when the cell is removed.

Curve (*a*)—Plate of ruby glass (flashed). Thickness 2.1 mm. The glass, when viewed edge on, was, unfortunately, of a greenish color, hence the transmission in the deep red was not as great as it

[1] A. H. Pfund.—Physical Review, Mar., *34*, p. 228 (1912).

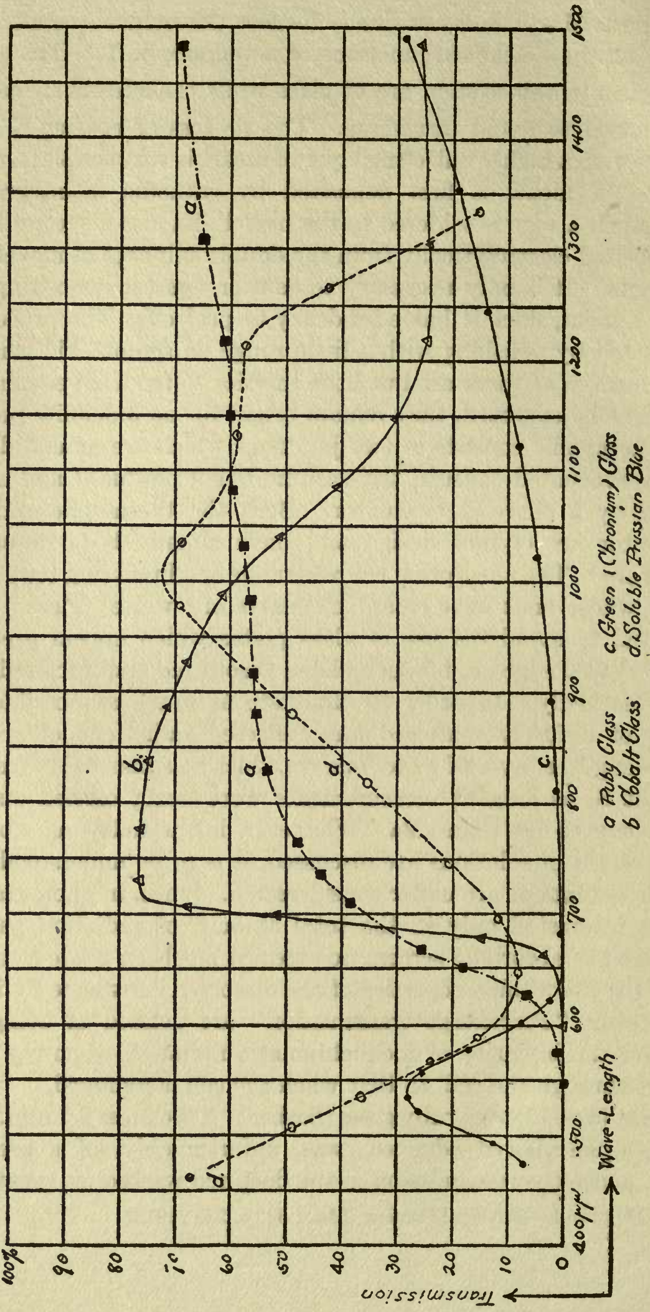

a Ruby Glass
b Cobalt Glass
c. Green 1 (Chromium) Glass
d. Soluble Prussian Blue
a
b.
c.
d.
Wave-Length
Transmission
400μμ
500
600
700
800
900
1000
1100
1200
1300
1400
1500
0
10
20
30
40
50
60
70
80
90
100%

Fig 3

would have been had colorless glass been used in the process of manufacture. Appreciable transmission begins at about 0.57μ, from where on it increases gradually—never attaining a very high value. Although this kind of glass is often employed as a filter for red rays it is not to be recommended since better filters are now available.

Curve (*b*)—Plate of cobalt glass. Thickness 2.2 mm. While not shown in the figure,[1] this glass is very transparent for blue and violet rays and has, in addition, smaller bands of transmission in the green and orange. In the red, the region of marked transparency begins at 0.65μ and rises very abruptly to a maximum at 0.72μ. By combining a sheet of this glass with a gelatine film containing a deep orange analin dye, Wood[2] succeeded in producing a very good transmission screen for infra-red photography.

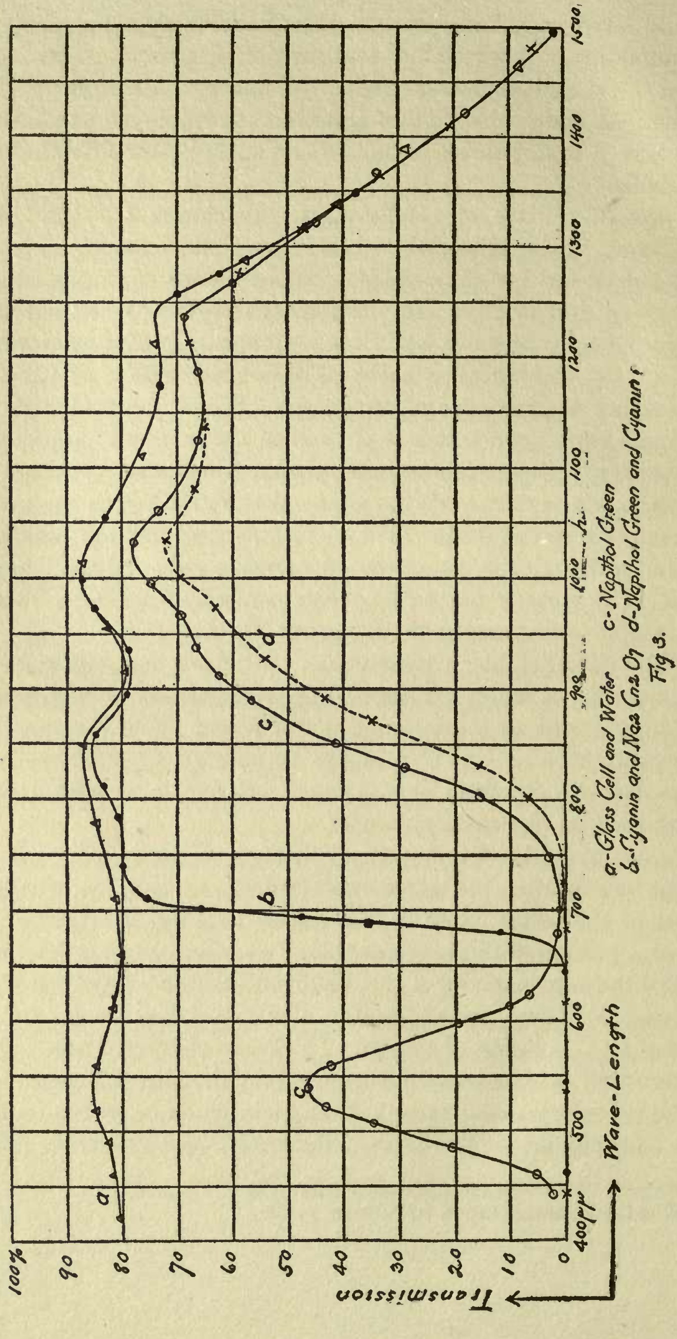
Curve (*c*)—Green (chromium) glass. Thickness 1.2 mm. The transmission is only very moderate in the visible spectrum where a maximum lies at 0.54μ. The violet and deep red are practically cut out although the transparency increases very gradually beyond 0.7μ. The glass is not to be recommended, either as a filter for green light or as a means of cutting out the infra-red.

Curve (*d*)—Soluble Prussian blue. Strength of solution 0.02%. Thickness of layer, 2.0 mm. The transparency is very great in the blue, drops to a minimum at 0.65μ and again increases to a maximum at 1.1μ. As a means of obtaining a filter for the radiations near 1.μ Prussian blue is much inferior to naphthol green, which will be discussed presently.

Curve (*a*)—Distilled water. Thickness of layer 2δ. mm. As might be expected, the transmission is high, up to 1.24μ, where the effect of the water band at 1.5μ begins to make itself felt. This curve is presented to make possible, if ever desirable, a determination of the transparency of the dissolved substances by themselves.

Curve (*b*)—Two parts of a 10% solution of $Na_2\ Cr_2\ O_7$ and one part of a 1% solution of cyanin. Thickness of layer, 2 mm. Cyanin by itself is extremely transparent in the violet hence it was found necessary to add some sodium bichromate in order to destroy this transparency. The latter substance is not only very opaque

[1] Uhler & Wood.—Atlas of Absorption Spectra, Z. C., p. 51.
[2] Wood.—Physical Optics, 2d Edition, p. 625.



a-Glass Cell and Water
b-Cyanin and Na2 Cr2 O7
c-Napthol Green
d-Napthol Green and Cyanin

Fig 3.

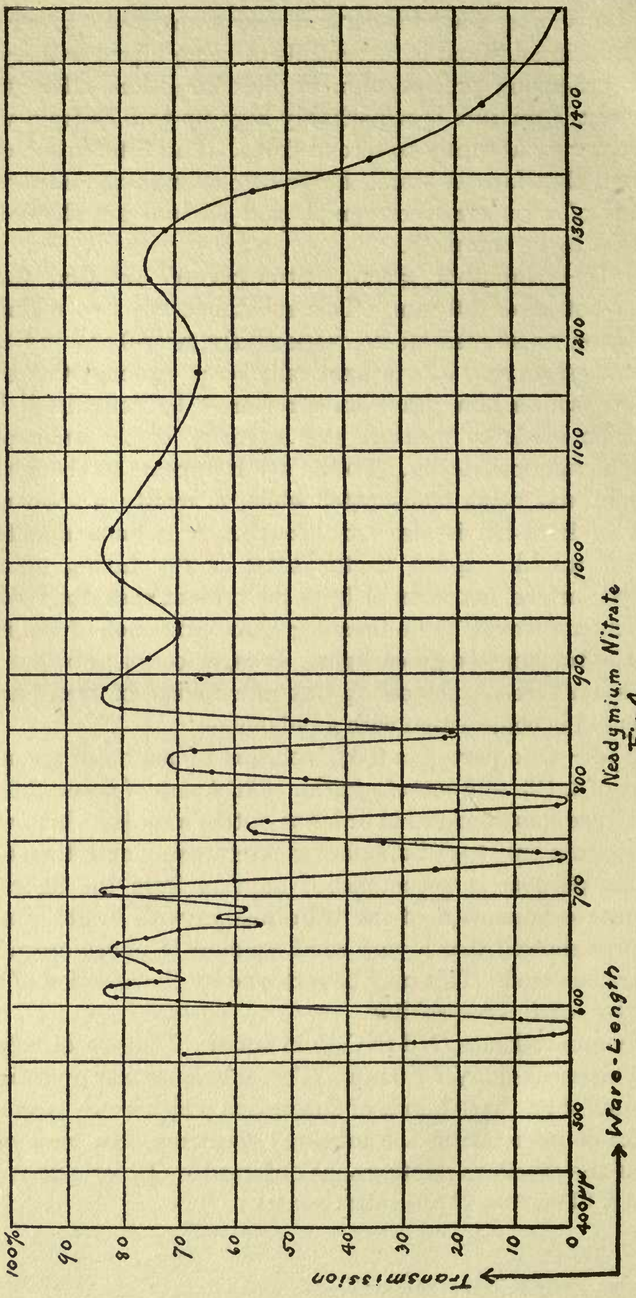
toward the shorter wave-length and very transparent toward the longer, but, in addition, is susceptible of being mixed with cyanin without producing precipitation or decomposition. The transmission of the mixture is remarkably high up to 0.7μ from where on it drops very abruptly to zero at 0.64μ. This filter is one of the best found thus far. A search for transmission in the ultra-violet by means of a quartz-spectrograph and an iron arc showed the absorption to be complete.

Curve (*c*)—Naphthol green. Strength of solution 0.07%. Thickness of layer 2.0 mm. This substance has two regions of transmission whose maxima lie, respectively, near 0.54μ and 1.03μ. The transmission near 0.7μ is practically zero. Among other things this curve shows how grave an error may be committed if an attempt be made to measure the intensity of the transmitted green light radiometrically. To the eye it appears as though only green light was being transmitted while, in reality, a tremendous amount of infra-red is also let through. A radiomicrometer or bolometer would respond to the total energy falling upon its blackened surface, hence, in at least the present case, the recorded measurements would by no means give an indication of the intensity of the transmitted green light. It is, of course, obvious that transmission screens possessing but one region of transparency may be used in conjunction with a radiometer.

Curve (*d*)—One part of a 0.6% solution of naphthol green and one part of a 1% solution of cyanin. Thickness of layer, 2.0 mm. This mixture was prepared in order to obtain a screen which would be transparent only to radiations of greater wave-length than 0.75μ. That this purpose is accomplished appears from the figure. A subsequent examination of the transmission with bright sunlight as a source showed that a very small amount of bluish-green light is also transmitted. This may be removed by the addition of some orange dye, such as crysoidine.

Neodymium nitrate ($Nd\,[NO_3]_3$) in water. Density of solution 1.75. Thickness of layer 2.0 mm. This substance was investigated on account of its sharp bands of absorption which serve excellently as marks of reference in the infra-red spectrum. In view of the fact that the excellent photographs obtained by Uhler[1] and Ander-

[1] Wood & Uhler, Atlas of Absorption Spectra.



Neodymium Nitrate
Fig. 4

son[1] are available, the present investigation was not carried through the entire visible spectrum. It was found that the principal absorption bands in the region of greater wave-length lie at 0.580μ, 0.735μ, 0.785μ, and 0.845μ. Due to the finiteness of width of the spectrometer slits and a slight imperfection of figure of the mirrors M_2 and M_3, the results obtained show the bands to be somewhat wider than they are in reality. This defect in the apparatus will not, however, interfere with a fairly accurate determination of the wave-lengths of the strong absorption bands. The absorption of a small cube of "didymium" glass was also investigated and it was found that while the general character of the absorption spectrum was similar to that of $Nd(NO_3)_3$ the bands of absorption were shifted markedly toward the red. The actual curve is not plotted since it probably applies only to the present specimen and hence there is no guarantee that the recorded positions of the absorption bands would hold for all kinds of didymium glass.

For the sake of completeness it may be added that whenever it becomes desirable to make use of the visible spectrum only and to eliminate completely the infra-red, nothing is better than a solution of $CuCl_2$[2] in water.

[1] Jones & Anderson. Carnegie Institution Monograph.
[2] W. W. Coblentz,—Bulletin of the Bureau of Standards, Vol. 7, No. 4, p. 659

GENERAL INDEX
TO THE TWENTY-FOUR VOLUMES OF ORIGINAL COMMUNICATIONS