CASEIN

ITS PREPARATION AND TECHNICAL UTILISATION

ROBERT SCHERER

THIRD REVISED EDITION

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BY

ROBERT SCHERER
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PREFACE TO THIRD EDITION.

For many years the sole use found for milk curd was in the manufacture of cheese to be used as a foodstuff. Skimmed or separated milk, produced in large quantities as a by-product in butter-making, was fed to pigs or even run into a stream. It is only through the scientific researches of the past few decades that the true value of albuminoid substances has been realised and that the manufacture of casein from skim milk has become a practicable proposition. Incidentally to this, the preparation of milk sugar has become a possibility, and the easy digestibility of this product has resulted in its being used in infants' foods and similar preparations.

It is easy to understand that our knowledge of casein is somewhat imperfect, especially as regards its manifold uses, but as time goes on it will become more and more appreciated in industrial applications since it has valuable properties which are not easily found in any other product. Communications on the subject in the technical press are rare, consequently it appeared desirable to the reviser to prepare a work dealing with this material.

The first part of this book treats upon the preparation of curd from milk, by decomposition of the suspended casein compound with acids or with rennet, and the purification and drying of the precipitated casein. Following this, the composition, properties, and reactions of casein are touched upon; then follows a description of the use of casein in the manufacture of paints, distempers, putties, plastic masses, artificial ivory, and other materials; the modes of applying these and their special features. The use of casein as a dressing for paper and cloth and its employment for waterproofing and other purposes is also described, and finally there are chapters on the use of casein in nutrient preparations, and the compounds of casein employed for medicinal purposes.

In compiling this work the reviser has endeavoured to bring together as much useful information as possible, and acknowledges his indebtedness to many investigators who are mentioned in the text and footnotes.

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CHAPTER I.

INTRODUCTION.

ALTHOUGH casein, in the form of cheese, has from time immemorial played an important part in the dietary of the human race, and has been produced in very large quantities, the technical utilisation of this product was almost entirely neglected. The property which it has of dissolving in alkaline liquids and forming, in this condition, a good mucilage, has long been known; but this was all, and it is only within a comparatively short space of time that any extensive technical application of casein has been made.

Casein is now used as a paint, as a dressing for textiles, a cement and mucilage, in the production of plastic masses, for sizing paper, and various other purposes. Since close attention has been bestowed on the action of formaldehyde on casein, a whole series of new uses has been discovered for the article, which is undoubtedly destined to play a very important part in technology. Furthermore, the original application of it as a foodstuff has not been lost sight of; its high nutritive value and its easy assimilability having led to the preparation of a number of artificial foods which are now extensively consumed. In cases where, owing to lack of means of communication, milk cannot be sent to large centres of population for consumption, it is now converted into butter and casein, the latter being disposed of for technical purposes.

In America considerable importance is attached to the manufacture and treatment of casein. It already forms an important article of commerce there, especially in papermaking, the manufacture of sized papers, and in painting and calcomining, and so forth ; but for these purposes production on a large scale is indispensable. Owing to the highly diversified uses of casein, those of a technical character being naturally the first to be considered, it seemed desirable to divide the present work into a series of chapters, each complete in itself, as follows :—

The preparation and properties of casein ; followed by its application :—

As a painting material ;

As a mucilage and cement ;

In the preparation of plastic masses, to be used as substitutes for horn, ivory, celluloid, etc., with special attention to "Galalith";

As a dressing and colour-fixing medium in the textile industry ;

As a foodstuff ; and for other various purposes which do not come within the other groups.

Finally, a summary will be given of most of the known compounds of casein with chemical elements, their salts, etc., and organic compounds which may become useful in course of time. The scattered literature of the subject has been consulted, and quotations have been made where they served a useful purpose.

CHAPTER II.

CASEIN: ITS ORIGIN, PREPARATION AND PROPERTIES.

THE milk of mammiferous animals, from which casein is derived, is a normal secretion of the healthy lacteal glands of the female animal. After the flow of colostrum (the first milk secretion after parturition) has ceased, normal milk is produced for a certain time, which is known as the period of lactation. Speaking generally, varying with the species, the milk of mammals is an opaque, whitish, or faintly yellow liquid, exhibiting a peculiar specific taste and smell. It consists of water, fat, casein, albumin, milk sugar and inorganic constituents, the most important being the fat and casein. Cows' milk is by far the most important, the solid matter consisting, according to Kirchner, of :—

	Average.	Min.	Max.
Fat	3·4 per cent.	0·8	to 8·0 per cent.
Casein	3·2 „	2·0	„ 4·5 „
Albumin	0·6 „	0·2	„ 0·8 „
Lactoprotein . .	0·1 „	0·08	„ 0·35 „
Milk sugar . .	4·5 „	0·3	„ 6·0 „
Ash	0·7 „	0·6	„ 0·9 „

The average composition of milk, according to Kœnig, is :—

Specific gravity	1·0316
Water	87·27
Casein	3·02
Albumin	0·53
Fat	3·64
Milk sugar	4·88
Ash	0·71

Milk must be regarded as an emulsion, *i.e.*, a heterogeneous liquid containing substances in suspension in a very finely divided state, and we must assume that the fat globules —the future butter—for instance, are surrounded by colloidal envelopes. The liquid fat globules attract substances dissolved in the milk and condense the same around themselves, so that we may safely assume that every fat globule is surrounded by an envelope richer in dissolved substances than the milk itself.

The Preparation of Casein.—When fresh, whole milk is left at rest, or is subjected to very rapid rotary motion by means of special appliances (centrifugal machines), the cream, or portion richest in fat, rises to the surface, and if this be skimmed off, skim milk is left. This latter forms the raw material for the preparation of the second chief product of milk, namely, the casein, which is present to the extent of 2 to 4·5 per cent., the average being 3·2 per cent. Casein is not dissolved in the milk, but is suspended in a state of distension, which can be proved by a simple experiment. If milk be filtered through a porous earthenware plate, the filtrate obtained consists merely of a solution of milk sugar and saline constituents, the fat and casein, neither of which is in solution, being left behind on the surface of the filter.

According to A. W. Bosworth and L. L. Van Slyke,[1] the residue left on passing milk through a Chamberland filter was composed of calcium caseinate (Casein – Ca_4) and neutral dicalcium phosphate.

The behaviour of milk under various conditions is determined by this peculiar condition of the casein present. This is the cause of certain physical properties of the milk, notably the viscosity, which in turn influences the rate at which the cream rises. The condition of the casein is not altered by warming or boiling the milk ; but, on the other hand, it is

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[1] "Jour. Bio. Chem.," 1914, **19**, 67-71.

precipitated by dilute acids or rennet. The precipitated casein is insoluble in water or dilute acids, and forms when dried a crumbling, horny mass; but it is dissolved by alkalis and concentrated acids. This behaviour of casein leads to the conclusion that it does not exist in a pure state in milk; and, in fact, experiments have shown that it occurs therein as a compound of lime containing 1·55 per cent. of CaO. According to H. Droop Richmond, it is held in solution by sodium calcium phosphate. This circumstance explains its behaviour towards dilute acids, *i.e.*, its precipitation thereby, the lime being extracted by the reagent and the casein left in the solid form. Only a very small quantity of acid is needed to effect this precipitation, 1 per cent. of lactic acid (from the milk sugar) being sufficient to curdle the milk. In addition to casein, small quantities of albumin (0·6 per cent.), lactoglobulin (traces), and lactoprotein are also present. Hammersten states that there are three proteids in milk: *viz.*, casein, lactalbumin, and globulin, the former constituting by far the larger proportion, amounting to about 80 per cent. of the total. Owing to the force of circumstances, it is seldom that casein products are prepared in the same place as the crude casein is produced, the raw material being generally obtained from dairies at a distance. For this reason the description of the mode of preparing the crude casein will be confined to the indispensable minimum.

Casein belongs to the group of animal albumins, compounds of carbon, hydrogen, oxygen, nitrogen, and sulphur, of which it may be said that comparatively little is known of their exact constitution. There are a number of these substances known, differing from one another in their general properties. White of egg, blood albumin, and the casein of milk, are examples; they have been the object of much investigation at the hands of chemists, although very little that is absolutely certain is known of them. In milk there exists, first, the fat which forms the basis of butter, then a small quantity of sugar, and, in pseudo-solution, a nitrogenous substance to which the name of casein is given. This product may be precipitated out by the addition of a little acid or by some metallic salt. When the precipitation is brought about by the action of rennet on ordinary milk, all the casein and fat are thrown out together, and the product pressed forms the foodstuff, cheese. If, however, by the use of separating machines the fat is first extracted as butter, then on precipitation almost pure casein is obtained. It may be noted here that the action of rennet is somewhat different to that of acids, inasmuch as the former does not completely throw down the casein, but leaves a certain proportion in solution. It is believed by Halliburton that the casein does not exist as such in the milk, but in the form of caseinogen. When the ferment rennet is added it is split up into casein and albumin; the former is thrown out as curds, the latter remaining in solution. When acid is used, all the caseinogen is converted into casein. The casein of commerce is obtained from separated milk by precipitation with acid. At present the great bulk comes from America, but some also from Scandinavian countries. Little, if any, is made in this country, because there is such a great demand for milk as a food product, that there is little, if any, surplus left for the manufacture of casein. While but little is known as to the caseins from various animal milks, yet it is quite evident they vary a little in some respects, although closely resembling one another in many properties (see p. 43). Casein comes into commerce as a yellowish-tinted, crumbly powder. It is here that it has an advantage over glue, for the latter is not obtainable in the form of a powder, and it is this difference that enables dry powder distempers to be made and sold, when casein forms a binder. It is nearly insoluble in water but dissolves more readily than glue when properly treated; alkalies like soda, caustic soda, and lime, facilitate the solution, and so dry slaked lime is one of the constituents of distemper. On exposure to the air this lime is converted into carbonate, the casein separating out and exerting a binding effect on the pigment. Casein alone does not produce a reliable washable distemper, although it helps considerably; the presence of a little linseed oil is needed, which, when used in the paint, oxidises and binds the pigment firmly. In a dry condition casein will keep for a long time, but when moist, like all other nitrogenous bodies, it undergoes putrefactive decomposition, to prevent which there may be added preservatives such as carbolic acid, thymol, salicylic acid, zinc sulphate, or zinc chloride.

Casein is recovered from skim milk (whole milk containing too much valuable butter to be used for the purpose) by throwing down the suspended substance with suitable reagents. These may be of two kinds. On the one hand, as already mentioned, acids, including the lactic acid formed as a fermentation product of the milk sugar, will curdle the milk and thus precipitate the casein; and, on the other, the same result can be brought about by the use of certain ferments, of which the rennet ferment, or lab, is the chief. At one time the product was regarded as the same in both cases, but careful experiment has shown that a considerable difference exists between them, pure casein being obtained when acids are used, whereas rennet furnishes the so-called paracasein, a fission product of the ordinary substance. Hence it is necessary to regard the two reagents as distinct in their action, this being a point of special importance when cheese-making is in question.

In order to secure the correct precipitation of the casein the milk must be kept at a certain temperature, not exceeding 140° F. nor lower than 68° F., since beyond these limits the action of the rennet is weakened and very imperfect. The milk may be warmed either by direct fire heat or by steam, a jacketed pan being used in the latter case.

Rennet is an enzyme which is generated by special glands in the stomachs of many animals, and is especially plentiful in the case of young animals. The rennet used in cheese-making is obtained from the stomach of the calf which is dried at the ordinary temperature, comminuted, and then extracted with a 5 per cent. solution of common salt, which dissolves the enzyme.

A small quantity of this fluid rennet, added to a large volume of milk, causes it to coagulate, forming a thick *curd* and a thin fluid or *whey*. According to Söldner, 1 part of rennet is capable of precipitating one hundred million parts of casein, a more moderate estimate by Hammarsten places it at 400,000 times.

Hammarsten[1] proved that the enzyme present in rennet differed from pepsin, and according to this authority it has a specific action upon the casein in milk, splitting it into paracasein, which is insoluble, and a smaller proportion of lacto-protein, which is soluble and passes into the whey.

That the coagulation of milk by rennet, although favoured by an acid, is not due to the generation of acid, was proved by Berzelius,[2] and later confirmed by Selim,[3] Lehmann,[4] Heintz,[5] and Voelcker.[6]

Schreiner[7] discovered the remarkable fact that milk which has been boiled is not coagulated by rennet. This was difficult to explain, but several years later Fr. Söldner[8] gave

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[1] Maly's "Jahresbu. f. Tierchemie," 1872, II, 118.

[2] "Lehrbuch der Chemie," 1840.

[3] "Jour. de Pharm. et de Chim.," 1846, X, 458.

[4] "Lehrbuch der Phys. Chem.," Leipzig, 1842.

[5] "Jour. f. prakt. Chem.," 1872, **6**, 374.

[6] "Jour. Roy. Agric. Soc. of Eng.," 1861, **22**, 61.

[7] "Chem. Centr." 1878, 588.

[8] "D. Landw. Versuchs-Stationen," 1888, **35**, 351.

the solution by showing that rennet was active only in presence of soluble salts of lime which were present in unboiled milk but largely precipitated out on boiling. An addition of a little alkali similarly causes precipitation of the lime salts and thus inhibits the coagulative effect of the enzyme. Milk deficient in calcium salts also requires a longer time for coagulation by rennet, but this can be remedied by adding a very small quantity of calcium chloride. Lindet[1] expresses the view that the calcium chloride thus added acts upon the alkaline phosphates and citrates present in the milk, which are solvents of the casein, with the formation of insoluble calcium salts, the casein being then thrown out of solution. The effect of the enzyme is not immediately perceptible and is influenced very materially by the temperature. It is most active at 37° C., as shown by A. Mayer,[2] but its action slows down either by cooling or by further heating; at 25° C. it requires three times as long to cause coagulation and only 18 per cent. of the casein is curdled; at 45° C. the enzyme is again less active; at 50° C. only 50 per cent. of the casein is curdled, while at 70° C. the enzyme is permanently destroyed.

The coagulation of milk by rennet has been the subject of much speculation recently, and several new views of the mechanism of the process have been put forward. Mellanby[3] assumes that the rennet enzyme is adsorbed by the casein and that the casein-rennet complex is precipitated by the calcium (bivalent) ions contained in the milk, the amount of ionised calcium salt required bearing a distinct relation to the quantity of enzyme adsorbed. Bang[4] draws the conclusion from his experiments that rennet is not *per se* a

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[1] "Compt. Rend.," 1913, 157, 381.

[2] "D. Landw. Versuchs-Stationen," 1882, **27**, 27.

[3] "Jour. of Physiol.," 1912, **45**, 345.

[4] "Skand. Archiv. Physiol.," 1911, **25**, 105-144.

coagulating enzyme, the actual curdling more nearly resembling the precipitation of protein by neutral salts than actual coagulation. Alexander[1] expressed the opinion that the casein in milk is "protected" or held in colloidal solution by the hydrophile colloid—lact-albumin—which combination is destroyed by rennet, the casein particles then coalescing into larger aggregates, which are then precipitated. Schryver[2] draws an analogy between sodium cholate and milk. He states that when calcium salts are added to sodium cholate and the mixture is heated a clot is formed. This clotting being influenced more or less by added salts. Thus salts which increase the surface tension of water decrease the time of clotting proportionately to the concentration of the salt. Salts which decrease the surface tension of water, on the other hand, decrease the time of clotting up to a certain limit of concentration, above which the opposite effect is produced, the time being increased or clotting entirely prevented. This inhibition of coagulation is regarded as due to the adsorption of simple molecules of the salt by the complex colloid, which is, therefore, held in colloidal solution by their power to prevent coalescence.

The same explanation holds good in the case of milk, the simple molecules of the salts being adsorbed by the casein, which is thus prevented from coalescing. The addition of the enzyme removes the adsorbed substances from the surface of the colloid, thus allowing the casein to coalesce and thus precipitate. Schryver assumes that in milk the condition of the milk and the clotting are due to four distinct classes of substances—colloids, calcium salts, simple inhibitory bodies, and enzymes.[3]

Preparation of Casein.—Leaving out of consideration the

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[1] "Proc. 8th Int. Cong. Appl. Chem.," 1912, **6**, 12-14.

[2] "Proc. Roy. Soc.," 1913, B **86**, pp. 460-481.

[3] "Second Report on Colloid Chemistry," Brit. Assoc., 1919, 100-105.

primitive pans, suspended over a wood fire, reference will be made only to the form shown in Fig. 1, which represents a pan surrounded by brickwork (*a*) with an annular flue (*b*) between the pan and the brickwork. To the right of the pan is mounted another, for heating the water, while a portable grate runs along a track (*h*), so that it can be rolled under one or the other pan as may be desired.

When used for heating the water pan a door at (*i*) fitted with a damper is closed. This arrangement offers numerous advantages, the height to which the flame is admitted in the flue, for instance, being controlled by a damper, whilst the surrounding brick setting enables the milk to retain the heat better than if merely suspended over an open fire. Finally, the fuel is more fully utilised, since none is uselessly consumed, the excess heat being employed for heating water.

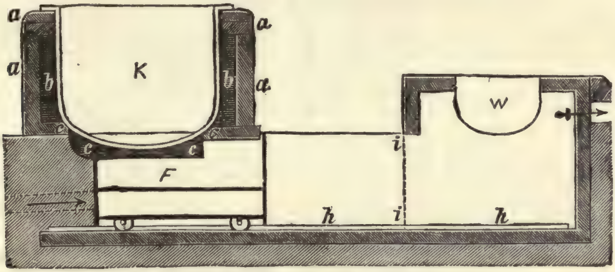

FIG. 1.—Heating Pan for the Preparation of Casein.
(*K* = Milk Pan. *W* = Water Pan. *F* = Portable Grate.)

Steam, or even hot water, can also be used for heating the pans, a steam pan of this character being illustrated in Fig. 2. The advantage in this case is that the heating surface exposed to the steam is very large, which, therefore, utilises the heat fully. A very useful form of pan is the "duplicator" (Fig. 3) for casein, jam boiling, and for evaporating or cooling milk, etc. It consists of two copper pans (of one-eighth to one-twelfth inch sheet copper), mounted in an iron frame, so that the whole can be tilted. The trunnions are hollow, to admit steam on the one side and cold water on the other, branches from the trunnions entering the jacket space and terminating in perforated pipes to ensure more perfect distribution of heat. *D* represents the steam valve, *W* the water tap, and *C* the discharge tap. The cold water runs away through the overflow, *Ue*.

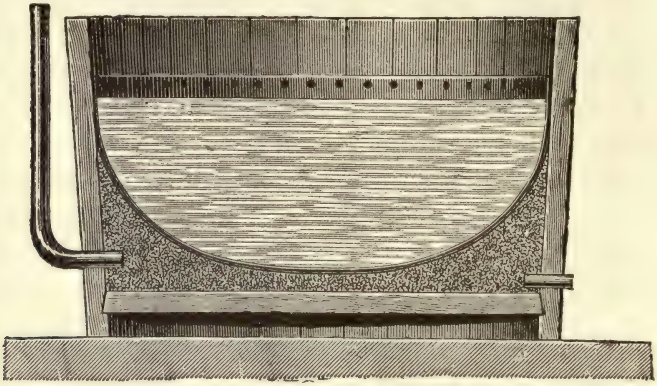

FIG. 2.—Steam Pan for Casein.

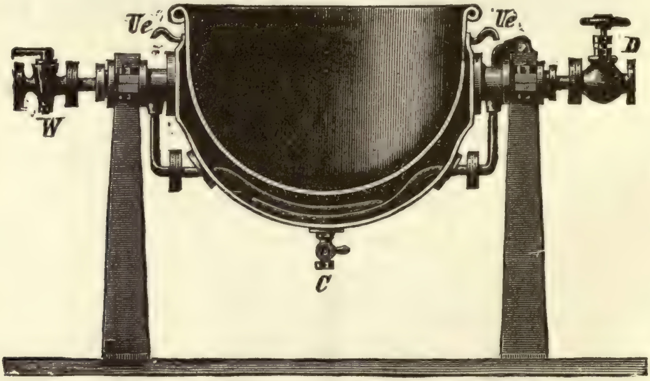

FIG. 3.—"Duplicator" Pan for Casein.

No special boiler is needed for generating the necessary steam, as high steam pressure is not required. A very convenient steam generator for this purpose is shown at Fig. 4.

Where water can be drawn from the mains the boiler is filled through the pipe (*a*). The steam leaves through the pipe (*B*), which can be fitted with several branch cocks, as shown in the figure leading to the different pans. The pipe (*c*), which extends to within four inches of the bottom of the boiler, serves a dual purpose. In the first place, it acts as a safety valve, the water being forced out if the internal pressure becomes excessive owing to obstructions in the outlet pipes. Secondly, if the boiler is not kept properly filled steam will escape through this pipe as soon as the water-level sinks below the lower orifice, an indication being thus given that the water requires replenishing. The piece marked (*d*) is a ground block of iron, fitting into a manhole, through which the boiler is cleaned out. It also acts as a safety-valve

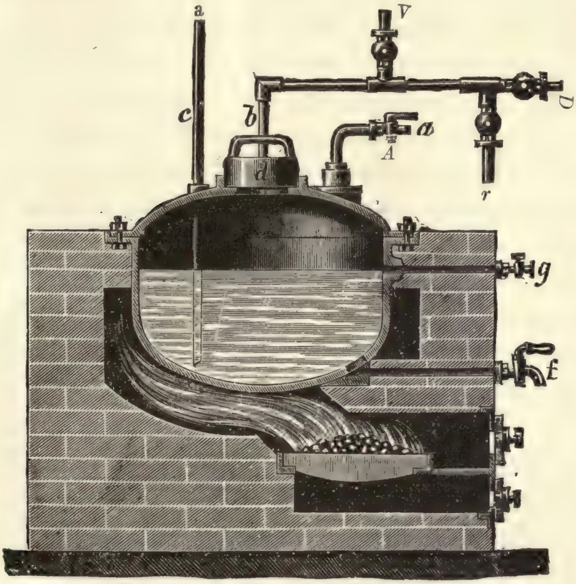

Fig. 4.—Steam Generator.
(*V* = Pipe to Casein Pan. *A* = Steampipe. *E* = Washer.
D = Fodder Steamer. *r* = Extra Branch.)

in the event of the pipe (*c*) getting choked. Hot water can be drawn from the boiler through the tap (*f*), which may also be used for the introduction of flushing water when the boiler is being cleaned. The pipe (*g*) is employed as an overflow in filling the boiler, to prevent over-filling, and indicates when sufficient water has been run in.

When the milk to be curdled has been raised to the proper temperature in one of the pans just described, it is treated with the rennet. No immediate change is apparent, but after some little time the milk begins to curdle, having thickened just before, and the precipitation of the casein is soon complete. At a temperature of 95° F. one part of good rennet is sufficient to curdle 10,000 parts of milk within forty minutes, whilst two parts will effect the same result in half the time or curdle double the quantity in the same time. For a given temperature and a definite quantity of milk the time required for coagulation varies inversely with the amount of rennet used.

Rennet which has been used once looses its power almost entirely, it being difficult to curdle a fresh batch of milk with the whey from the previous one. From this it follows that the curdling of milk by rennet must be regarded as a very protracted chemical process, which does not become apparent until it has proceeded to a certain stage. The stronger the action of the rennet, and the sooner the casein is thrown down, the more powerful the contraction of the curd and the larger the volume of whey expressed. This means a reduction in the residual water in the curd and an increase in its final dryness and firmness. Hence the manner in which the rennet acts is of considerable importance in its effect on the character of the casein.

This latter is also influenced by the quantity of rennet used, the temperature at which it is allowed to act, and, finally, by the character of the milk, or, rather, the casein therein. The character of the casein reacts on the influence of the rennet, and the same applies to the reaction of the milk, an acid reaction favouring the working of the rennet, whilst an alkaline reaction retards or annuls it. In the case of normal milk, which has an amphoteric reaction, the action is intermediate between these two extremes. The increased effect in the case of sour milk is explained by the presence of a larger quantity of soluble salts of lime, which are essential to the action of the rennet. With an alkaline reaction the proportion of these salts is lower, and, consequently, the rennet is less efficacious. Cases have been known in which the imperfect action of rennet—resulting in the milk refusing to curdle at all—has been traced entirely to the poverty of the milk in soluble lime salts. Old milk, again, takes longer to curdle than when fresh; and the percentage of water present also plays a part. Milk that has been boiled, or heated to 167° C., is more difficult to curdle, and will not do so at all in some cases owing to the alteration effected in the lime salts by heat.

Lactalbumen and lactoglobulin are coagulated by boiling, in the same way as albumen and globulin. Casein, on the other hand, forms a skin on the surface of the milk due to evaporation, but does not coagulate below 266° F. in a closed vessel. The formation of the skin is prevented by stirring, or by heating the milk in an enclosed space or one saturated with steam.

As already mentioned, the decomposition of milk can be effected by other substances, particularly acid and acid salts; though these are rarely used, since the chief use of casein, in the form of cheese, is as a foodstuff.

The coagulation of milk furnishes two chief products: the curd, containing a larger or smaller proportion of fat, proteids, and lactic acid; and the whey, containing the soluable salts of the milk, together with some finely divided curd, lactic acid, milk sugar, etc. Strictly speaking, the whey can be differentiated into cheese-milk and whey, the former term being applied to the liquid remaining after the separation of the curd, whilst whey, in the narrower sense, is the residue left after the removal of the whey-butter and whey-cheese. The whey proper is used as a beverage, in baking, for feeding pigs, and also for the recovery of milk sugar (for alcohol or vinegar), and the preparation of fermented liquors, such as whey-champagne and whey-punch. The two classes of whey have, according to Fleischmann, the following composition :—

	Cheese-milk.	Whey.
Water	93·15	93·31
Fat	0·35	0·10
Proteids	1·00	0·27
Milk sugar and lactic acid	4·90	5·05
Ash	0·60	0·47

The casein separated from milk is termed "curd," and is subjected to further treatment, mainly with a view to reducing its water content when cheese-making is in question. If, on the other hand, it is to be used for technical purposes, it must be thoroughly freed from the residual whey by repeated washing with hot or cold water, and, finally, more or less thoroughly pressed (according to the purpose in view) to expel the water.

The spontaneous and artificial coagulation of milk has been dealt with by Prof. Pokorny ("Chemiker Zeitung") as follows: "It is known that milk left to stand becomes sour and curdles spontaneously as the result of the formation of acid. This cause is demonstrated by the fact that fresh milk can be curdled by the addition of lactic or other acid, the same result being produced by acid salts." When milk is allowed to stand at the ordinary temperature it becomes acid owing to the generation of lactic acid due to bacterial action on the lactose or milk sugar also present, and as soon as the acid reaches a certain concentration the milk curdles or forms a soft jelly. The reaction which takes place is not a simple one, since gases and other products are also formed, but the chief change is due to the absorption of the elements of water as follows :—

$$\underset{\text{Milk sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Lactic acid.}}{4C_3H_6O_3}.$$

The presence of an organism during lactic fermentation was first discovered by Pasteur,[1] who also showed that the addition of this organism to sweet sterile milk caused it to rapidly become sour. The organism was isolated in the form of a pure cultivation by Lister,[2] who used the now well-known method of dilution for the purpose, and named the organism *Bacterium lactis.* Hueffe[3] also prepared pure cultivations and examined the organism very closely, the name given to it by him being *Bacillus acidi-lactici.*[4]

Fresh milk treated with acetic acid is coagulated almost instantaneously when the amount of acid used is large, though with small quantities of acid some little time elapses before the flakes of casein can be observed adhering to the walls of the test-glass on shaking. Sulphuric acid, being a strong mineral acid, coagulates milk at once when added in the proportion of 5 per cent. (*e.g.*, 10 c.c. of 10 per cent. sulphuric acid to 20 c.c. of milk).

For commercial purposes either acetic or hydrochloric acid are used. The nature of the acid is not important in the clotting, which depends upon the hydrogen ion concentration, the time required for clotting, according to Michaelis and Mendelssohn,[5] being proportional to the latter.

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[1] "Compt. Rend.," 1857, **45**, 416.

[2] "Quart. Jour. Micros. Sci.," 1873, **13**, 380.

[3] "Chem. Centr.," 1884, 315.

[4] "Technical Mycology," 1910-11, by Dr. Franz Lafar.

[5] "Biochem. Zeit.," 1915, **58**, 315.

Alleman[1] gives the optimum hydrogen ion concentration as $2{\cdot}5 \times 10^{-5}$ and the minimum $1{\cdot}3 \times 10^{-5}$.

The first treatment of the curd in cheesemaking is designed to remove the enclosed whey, the curd being vigorously stirred or broken by hand with a curd-breaker or similar instrument. Curd mills are also used, these consisting principally of a grid or lattice of galvanised iron rods, between which rotates a shaft armed with teeth. When the shaft is turned by means of the handle, the curd introduced through a feed hopper is pressed between the rods by the teeth, and thoroughly broken up or squeezed. The broken curd is then stirred to a uniform pulp with a little water in a large vat, and passed through a sieve or mill, after which sufficient water is added to form a milky liquid. This is left for the curd to settle down, and sieved to drain off the liquid; or in large dairies it is put through a centrifugal separator.

All centrifugal machines are driven by steam or electricity, by means of intermediate gearing, or else by special driving mechanism, and have to be run at high speed, which in turn entails solidity of construction. For reasons of safety, therefore, the maximum permissible load and speed of rotation should be conspicuously posted on each centrifugal machine, and machines of this kind driven by attached motors should be provided with a speed indicator marked with the maximum permitted speed. These machines are either driven from above through a second motion mounted on uprights forming part of the machine, or else from below, the motion being transmitted to the vertical shaft, this latter method being now almost exclusively employed. Though both systems entail good construction and very careful supervision in working, this is particularly the case with overhead driving. They also require very strong foundations, the contents of the drum are very liable to contamination by the

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[1] "Biochem. Zeit.," 1912, **45**, 346-358.

lubricating oil, and the accessibility of the drum is greatly reduced by the main shaft passing through it. On the other hand, the machines take up less room than those driven from beneath. A typical centrifugal machine with bottom driving is that shown in Fig. 5, for which the maker claims the following points of superiority: (1) Perfectly even and noiseless running, combined with low cost of up-keep; (2) absence of any masonry foundation, which is replaced by a strong wooden frame, enabling the machine to be set up in any convenient place, even in upper storeys; (3) small consumption of motive power, drum perfectly clear inside; (4) driving mechanism situated under the drum, preventing any contamination of the contents by dropping oil; (5) careful and solid construction of the various parts, with minimum wear and tear; (6) high speed combined with perfect safety.

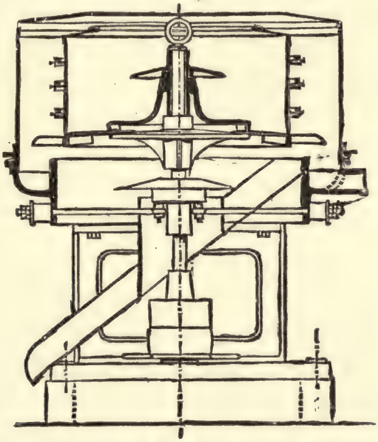


FIG. 5.—Section of Centrifugal Machine with Bottom Discharge.

The drums are constructed and arranged in such a manner that the contents are expelled with perfect regularity. They are usually made of sheet copper, though for other purposes use is made of steel, wrought or cast iron, and aluminium, brass, bronze, nickel plate or porcelain, or they are coated with vulcanite or enamel, as well as tinned, lead-lined, galvanised or silver-plated. A vulcanite lining is recommended for all materials which are injured by contact with metal, or where the metal used cannot properly resist the action of acids, etc. For these purposes vulcanite is superior to porcelain or earthenware linings on account of its lightness, a machine coated with it can be run at the highest speed permissible for centrifugal separators, whereas with earthenware the heavy weight necessitates low speeds. The same applies to lead-lined drums, in which, owing to technical difficulties, a uniform lining cannot be secured with sheet metal less than about one-eighth inch thick, thus making the drum so heavy that it cannot be run without danger at the ordinary speed.

The washing and draining of the curd is repeated several times, until the washings run away clear, the curd being finally drained in the separator and pressed, if necessary, to bring it to the proper state of dryness. In this form it can be sent out for some uses, in which the presence of the residual moisture is not detrimental; otherwise it is thoroughly dried for conversion into powder.

The drained curd may be dried on trays in drying-rooms, heated by a current of hot air to facilitate the removal of the moisture, or else is treated in special forms of apparatus, a few of which will now be described. The first of these is the drying cylinder, heated either from inside or outside, or both, and rotated to keep the contents in constant motion. The cylinder may be provided with a shaft carrying paddles or similar devices rotating in a fixed cylinder, or with the former stationary while the cylinder revolves; or the two may move in the same or opposite directions. The best type of drying cylinder is one containing no moving internal parts, since these parts are liable to become obstructed, and even broken, by the material under treatment when in large masses; and they also break the material down too small in some cases. The rotary movement of the cylinder or of the shaft not only keeps the material in a constant state of agitation, and thus greatly accelerates drying by presenting fresh surfaces for evaporation, but it also gradually moves the material onward in the cylinder. The operation, therefore, proceeds continuously, in the same way as in a drying flue, though more rapidly on account of the constant stirring, yielding a product of perfectly uniform dryness throughout. The progressive movement of the material is effected in various ways, either by means of an internal rotating shaft, fitted with spirally mounted arms, which therefore acts like a worm conveyer, or else by mounting the drum with one end higher than the other. The latter effect may be also obtained by the use of a conical casing, the shaft being mounted horizontally, though the cylindrical form, with the shaft tilted at an angle from the horizontal, is preferable, on account of lower cost and greater ease of manufacture. In this system the central shaft and arms are unnecessary, the drum being actuated by a toothed crown round the outer edge, driven by worm or cog gearing. Worm gearing is preferable, being more easily fitted and giving the requisite slow movement without any troublesome reducing gear when the shafting is run at the ordinary speed. In view of the small power needed to drive the cylinder, no objection on the score of useful effect applies to the use of worm gearing.

The interior of the cylinder must be fitted with blades, which lift up the material under treatment and allow it to fall again slowly and in small quantities, so that every particle is repeatedly exposed to the surrounding warm air. At the same time, the material is always lifted perpendicularly to the axis of the drum and falls vertically, thus describing a spiral line, the pitch of which depends on the slope of the drum axis towards the horizontal. Each revolution of the drum, therefore, moves every particle of the contents spirally onward, the rate of advance being regulated by two factors—the speed of the drum and the axial slope. If the latter be nil, the pitch of the aforesaid spiral will be also nil, and the material will be turned over but not moved forward : and in proportion as the axial slope is increased or diminished, so also will the material in the drum move faster or slower. Since the same drum is used for drying different materials at different times, or for treating the same material containing different percentages of moisture, it is advisable to make provision for working in a corresponding manner, which can be most easily done by making the axial slope adjustable. In this manner the onward movement of the material can be accelerated or retarded as required, and the drying process carried on in a uniform manner at the smallest expense. A few instances of typical drying cylinders will now be given, the details of which can be modified according to requirements.

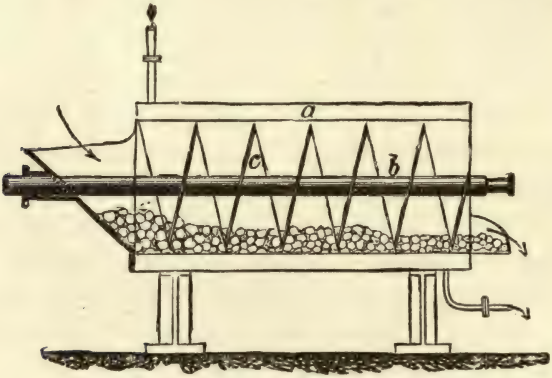


Fig. 6.—Rotary Drying Cylinder.

Fig. 6 represents a horizontal drum (*a*) fitted with a shaft (*b*), the arms (*c*) of which move the material onward. The cylinder is of the fixed type, and is jacketed for steam heating. The liberated moisture escapes through the discharge outlet.

The Passburg drying apparatus (Fig. 7) is fitted internally with a rotary system of tubes, which also serves to mix, advance, and dry the contents of the drum. The heating efficiency of this apparatus is high resulting in great drying capacity. It may be heated either by live or exhaust steam.

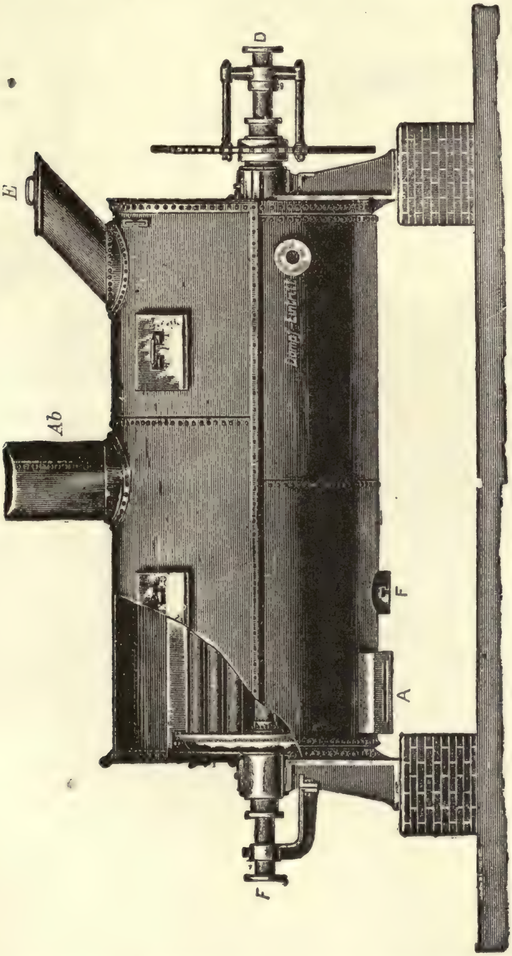


Fig. 7.—Passburg's Rotary Drier.

(*Ab* = Vapour Exhaust. *E* = Feed Pipe. *D* = Steam Admission. *F* = Waste Steam Outlet. *A* = Discharge Orifice.)

Fig. 8 shows the Patent Agitator Vacuum Drier made by Geo. Scott & Son (London), Ltd. In this form of drier the material is kept agitated by means of curved blades fixed to a central shaft which is caused to revolve by means of toothed wheels. The material is thus kept on the move and new material constantly exposed to the heated surfaces, at the same time the breaking up of the material allows the moisture to escape. The vacuum is obtained by the pump shown in the centre of the illustration.

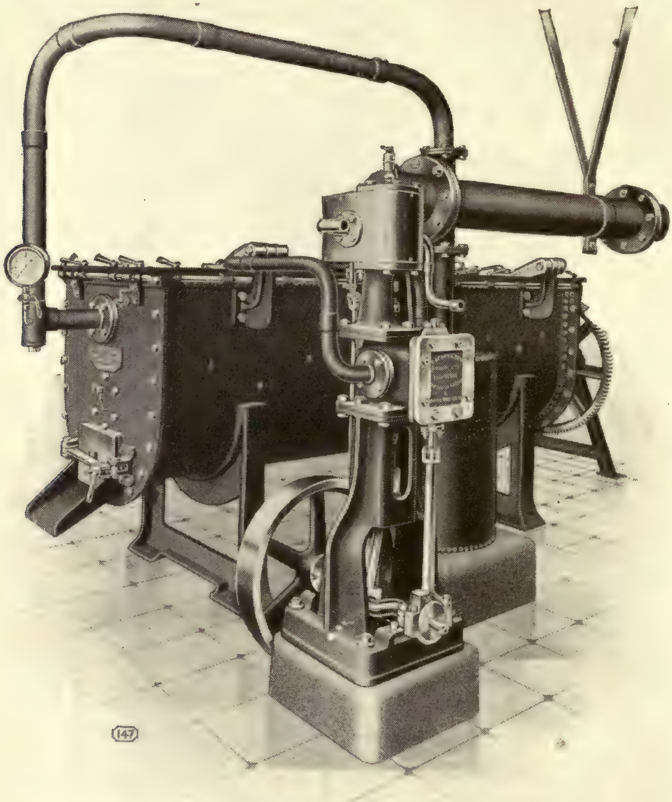


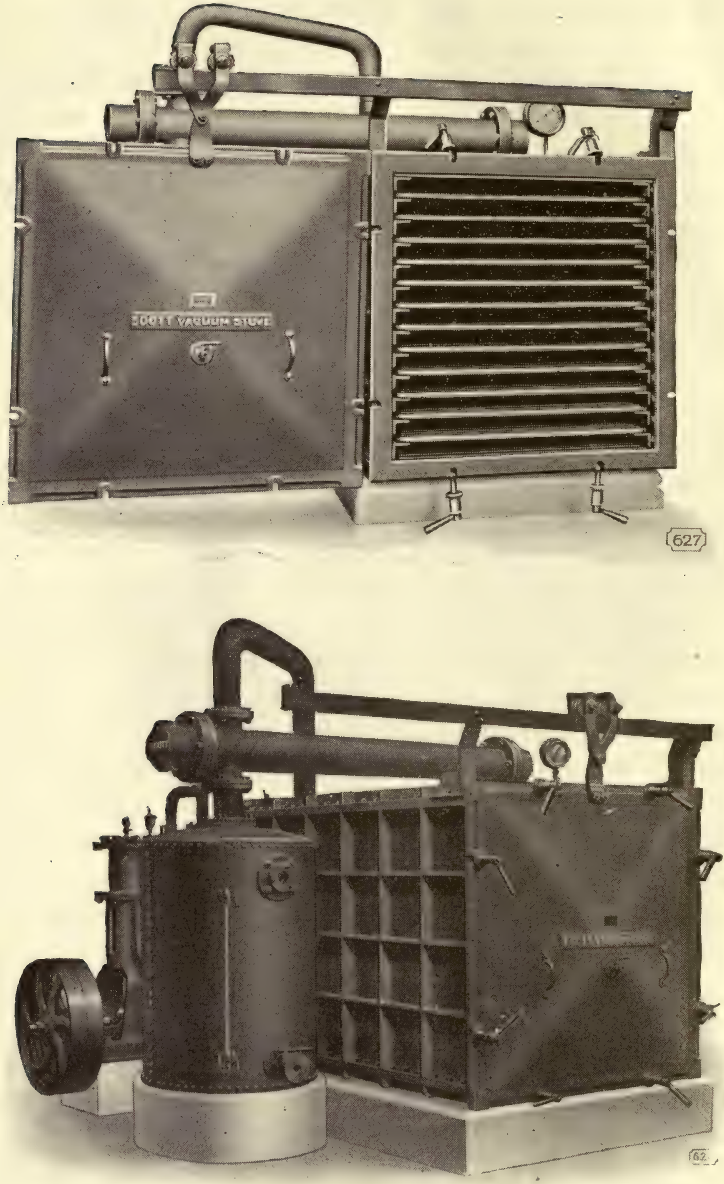
Fig. 8.—Patent Agitator Vacuum Drier. George Scott & Son, Ltd.

These rotary driers are suitable where economy in the first cost is the prime consideration. For some materials they have also a decided advantage over the shelf type of drier.

The vacuum drier, shown in Figs. 9 and 10, made by Geo. Scott & Son (London), Ltd., consists of a cast or wrought-iron case, which can be hermetically closed by a door at the front. The chamber is divided into a number of superimposed hollow steam shelves, fitted with proper connections for admitting and discharging the heating fluid, and constructed to stand a working pressure of 5 atmospheres. These shelves support the trays holding the material to be dried. When the rubber-shod doors have been closed, a vacuum of 720 mm. mercury gauge is produced in the chamber by means of an airpump, the shelves being meanwhile traversed by the steam or other heating fluid employed. In consequence of the vacuum the water in the material to be dried is vaporised readily and quickly at a comparatively moderate temperature (about 104° F.), so that drying is soon effected. In fact, the apparatus will dry in a few hours, and without the slightest risk of overheating, materials which being difficult to dry take several days when treated by other processes, even if they can be dried at all. The apparatus is easily and conveniently fed, and does its work in a clean and efficient manner. The temperature is regulated by simply adjusting the steampipe valve. When hot water is used for heating and an efficient vacuum is obtained by means of a vacuum pump, the water can be vaporised at 68° F.

Purifying the Curd.—One hundred parts by weight of well-pressed curd are stirred to a pulp with 50 parts of water, and, in order to remove lactic acid and butter fat, it is steamed for twenty-five to thirty minutes in a wooden vat together with about 150 parts of a 1 per cent. solution of bicarbonate of soda.

The vat must be of ample capacity, on account of the



Figs. 9 and 10.—Tray Vacuum Drier. George Scott & Son, Ltd.

frothing that occurs. After heating, the mass forms a thin milky liquid, which is transferred to a separate vessel to cool, and is then treated with dilute nitric acid until a small sample no longer exhibits traces of a precipitate. As a rule ½ to ¾ per cent. of 40 per cent. nitric acid, mixed with 4 parts by weight of water, will be sufficient. The casein separates out from the milky liquid on standing and falls to the bottom. The supernatant fluid is run off, the casein rinsed with fresh water, left to settle, the water decanted, and the washing repeated till the effluent water is perfectly neutral.

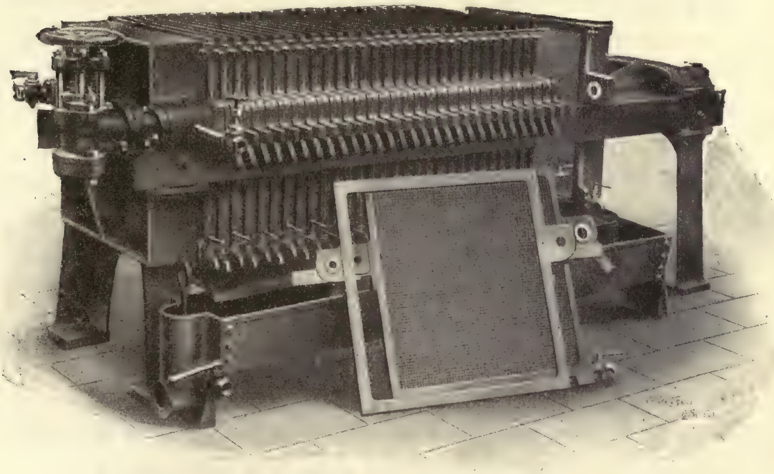


FIG. 11.—Jchnson's Filter Press.

To convert the casein into a dry powder it is laid on filter cloths to drain and afterwards pressed, preferably in a filter press (Fig. 11), this operation being followed by drying on trays in drying chambers at a temperature of 120° to 140° F. The finished product can either be worked up at once or may be stored in a dry place for use later. The small residual quantity of butter fat in the casein could be entirely removed by digestion with benzol or with an ether-alcohol mixture, but owing to the troublesome nature of the process it is seldom practised. One hundred parts of curd furnish 45 parts of purified casein, free from lactic acid and butter fat. The moist material can be immediately converted into a good glue by mixing it with 25 per cent. of distilled water and 1 to 4 per cent. of bicarbonate of soda in a mechanical stirring apparatus working at fifteen to twenty revolutions per minute. Afterwards another 25 per cent. of distilled water is added to complete the solution, and the whole is left to stand for five to six hours. At the end of that time the glue will be pliant and fit for use. An antiseptic is added to prevent mould.

A very similar process to this is claimed by R. Eilersen of Copenhagen (U.S. Pat. 1,126,429, March 19, 1914) in the preparation of casein from buttermilk, the buttermilk being heated to 40° to 65° C. until the curd separates. The latter is washed with cold water, and then a quantity of water about equal to the whey is added and sufficient bicarbonate of soda to dissolve the curd. The liquid is filtered to remove any butter fat and albumin which remain undissolved, and sufficient hydrochloric acid is added to render the liquid acid, whereupon the casein is precipitated, and, after washing with water is dried.

Owing to the difficulties of transport, it is in many cases impossible to distribute milk in a fresh condition. By converting it into casein, a dry non-decaying substance that may be packed in boxes or bags, it may be carried with ease, and it finds a ready sale for use as a substitute for celluloid, over which it has the advantage of not being inflammable. For some years a profitable business has been conducted at Anand in the Baroda State in the production of casein for export. The process resembles the manufacture of cheese. The skimmed milk is coagulated by rennet, precipitated by hydrochloric acid, and separated in a centrifugal filter. The result is a whitish or yellowish mass which is the casein of commerce. There are several ways of separating it, one of the most recent being by a current of electricity, which is said to be the cheapest where current from wind or water power is available.

Vegetable Casein.—At a meeting held at the Chemists Club, New York, Dr. Oskar Nagel, read a most interesting paper on vegetable protein, in which after describing the process used for the extraction of vegetable albumin, he proceeded to discuss the method of extracting casein from vegetable sources. He said : for making vegetable casein, which, in its solubility, viscosity, and other properties, is equal to milk casein, I use soy-bean, which, until now, has not been used in chemical industries. This seed, being the richest casein-containing seed produced by nature, and at the same time exceedingly cheap, can be imported from China in any quantity desired. It contains 12 to 18 per cent. of an excellent edible oil, largely used in the Orient, and 30 to 40 per cent. casein. The richness in fat decreases the expenses of the process considerably. For making casein the finely-ground beans are extracted nearly completely by means of benzine or any other solvent in an apparatus ordinarily in use for that purpose. Hydraulic presses may also be employed for removing the oil, but in this case the residuum will naturally be richer in fat than if worked by extraction. The residue, freed from benzine, is digested at a temperature of 30° to 35°, with a 5 per cent. solution of sodium carbonate for several hours, solution being assisted by means of stirrers. The solution is then filter-pressed.

The casein is now precipitated from the filtered alkaline casein solution, with continuous stirring, by means of rennet or a 5 per cent. solution of hydrochloric acid. The precipitated casein is filtered, washed, and dried in a steam-heated room at as low a temperature as possible. The benzine is removed in the extraction apparatus mentioned above, from the solution of oil in benzine, obtained in the first part of the process, and used over again.

CHAPTER III.

VARIOUS METHODS OF PREPARING CASEIN.

In order to obtain white casein, free from the yellow tinge attaching to that prepared with sulphuric acid, several different acids are used in succession as precipitants, a method which also has the advantage of cheapness. The best plan is to first throw down the casein as curd, with sulphuric acid, then dissolve this curd in alkali, and reprecipitate with acetic acid. According to the German patent specification of R. Hatmaker (dated May, 1901), about one and a half parts by volume of sulphuric acid (density 66° B.), diluted with seven of water, are sufficient to precipitate the curd from 1,000 parts of milk. If the operation is performed at a temperature of 100° to 120° F., the curd will come down as large and solid lumps, which must then be thoroughly washed with cold water. The curd from the above quantity of milk can be dissolved in 350 parts of a 5 per cent. solution of bicarbonate of soda, the process being accelerated by warming the whole to 100° F. Acetic acid of about 29 per cent. strength is used, and is added slowly till all the casein has been thrown down and the separated aqueous liquid is perfectly clear. After this liquid has been drawn off the casein is thoroughly washed with cold water.

A. Hall recommends that the milk should be curdled with hydrochloric acid, the resulting casein being heated to such a degree that the contained acid volatilises. A current of air is also passed through the mass. This would, however, lead to a certain amount of decomposition.

According to A. Spitteler, the alkali used in preparing the casein should be replaced by an alkali carbonate, when a colourless, tough casein is desired. In this case the reaction proceeds more gradually. Should a transparent product be desired, the separated substance should not be removed from the solution until the latter begins to be transparent.

K. Ruprecht states that the following method is employed for producing technical casein :—

Skim milk is placed in a vat fitted with stirrers consisting of a vertical shaft carrying several horizontal blades. These stirrers are set in motion so as to bring the whole of the liquid into rapid rotation, and dilute hydrochloric or acetic acid is run in by degrees. The casein begins to separate immediately in the form of tender white flakes, and the quantity of acid used is strictly limited to the amount necessary for precipitation ; while continuing the stirring a sample of the liquid is taken, filtered, and the clear filtrate tested with a little of the acid. If it remains clear, the whole of the casein has been precipitated.

The liquid is then allowed to stand until all the casein has settled down, whereupon the clear liquid may be syphoned off by means of a rubber tube fitted with a glass funnel, the mouth of which is covered with fine gauze, and is lowered into the liquid until it reaches the curd, which is kept back by the gauze sieve. The separated liquid contains albuminoid compounds, salts, and the whole of the milk sugar present in the milk, for the recovery of which it can subsequently be treated.

The caesin left in the vat is stirred up with water, left to settle, the water run off, and the operation repeated two or three times. The casein, thus sufficiently purified, is placed in strong filter cloths, which are placed between wooden plates in a screw press. Pressure is applied gradually and so long as any liquid continues to drop. The casein is next taken out of the cloths, and as it still contains a considerable amount of moisture, it is broken down into small lumps, which are spread out thinly on cloths stretched on frames. These are placed in a drying-room, kept at a temperature of about 86° F., until the casein is perfectly free from water and will crumble to powder under the pressure of the finger.

When thoroughly dry, casein can be packed and stored in a dry room for an indefinite period, without undergoing alteration. On the other hand, the presence of even the smallest quantity of moisture enables micro-organisms to develop in the casein which cause putrefaction of the whole mass. The following method is very suitable to adopt in packing casein. The dried product is spread on cloths and sprayed over with a small quantity of pure 95 per cent. alcohol, after which it is immediately packed tightly into square cardboard boxes, with a strip of paper pasted round the edge of the lid when closed. The minute quantity of spirit introduced into the casein volatilises, forming an atmosphere in which no micro-organisms can develop.

Casein prepared in this manner will gradually swell up, in very dilute solutions of caustic alkalies or their carbonates, to a transparent mass, and eventually pass into solution. The same result can be obtained without drying the casein, the solution keeping well and having the advantage of being ready for use without waiting for the solid casein to swell and dissolve. With this object the washed casein is mixed in the vat with sufficient water to form a thick cream, to which is added about a quarter of a pint of aqueous ammonia per pound of dry curd present. This can be calculated approximately from the weight of milk taken in the first place, the average casein content being 3·2 per cent. After adding the ammonia the vat is covered up and the stirrers kept in motion for some time; whereupon, if sufficient ammonia has been used, the casein will be found to have dissolved to a clear viscous liquid, with a faint yellow tinge. On the other hand, if the liquid is cloudy, more ammonia should be added, with stirring, until the solution becomes clear. The finished solution is then run into glass bottles at once and hermetically sealed. After prolonged standing, a small deposit of undissolved casein may settle down in the bottles. This clarified solution when poured out on glass, dries to a hard, colourless and insoluble mass, with a high lustre, on which account it serves as an excellent lacquer. Printing colours that are not sensitive to the action of ammonia may be mixed and printed with the liquid, the casein becoming insoluble on evaporation, thus fixing the colour on the fabric.

A patent on the following lines, for preparing fat-free casein from skim milk, was taken out by Mierisch and Dr. Eberhardt. Ordinary "separated" milk contains 0·2 to 0·3 per cent. of fat, and if used for the preparation of casein, yields a product containing 6 to 8 per cent. of fat. The usual method of removing this fat is by extraction with fat solvents or repeated solution in alkalies and reprecipitation by acids; but in the patented process the skim milk is mixed with alkali, warmed and centrifugalised to expel the fat, the liquids being afterwards treated with acid, in the usual manner, to throw down the casein. For example, 100 gallons of skim milk are mixed with a solution of 2 to 4 lb. of caustic soda, the whole being warmed to 100° to 112° F. and put through the centrifugal separator until no more fat passes over. The casein is next thrown down with dilute sulphuric acid and collected, washed, pressed, and, if necessary, dried. The product thus formed will satisfy practical requirements in respect of freedom from fat.

Riegel's method of precipitating casein with ethylsulphuric acid is intended to replace the use of acetic acid, lactic acid, and sulphuric acid for this purpose. The acid in question shares with sulphuric and acetic acids the property of precipitating the casein in an undecomposed, compact, and non-mucilaginous form, but possesses the advantage that, owing to the ready solubility of its lime salt, the casein is obtained almost free from ash by the first precipitation. At the same time the casein is poorer in germs than when acetic acid or lactic acid is used, the inverting action on the milk sugar at the same time being smaller. Crude ethylsulphuric acid is used, this being prepared by rapidly mixing equal volumes of concentrated sulphuric acid and strong alcohol, and leaving the mixture to stand for several hours in a warm place.

To obtain soluble casein in the dry commercial state, the curd is thrown down from the milk, washed to remove whey and any excess of precipitant, dried at a moderate temperature to preclude risk of burning, granulated, and allowed to absorb a small quantity of dissolved alkali by rapidly stirring the two together. Finally, the granulated alkaline product is dried in accordance with American patent 664,318.

Szekely's patent (German patent 126,423) relates to the separation of milk into casein and whey by means of carbonic acid. For this purpose, sweet new milk, cream, skim milk or buttermilk is placed in a closed vessel, warmed somewhat above 86° F., and a sufficient amount of carbonic acid gas is forced in under pressure to precipitate the whole of the casein when well shaken or stirred.

To overcome the differences in skim milk in the separation of the casein, C. H. Bellamy of Philadelphia adds to the casein in the preparation of casein glue an alkali arsenate (*e.g.*, Na_2HAsO_4). This addition is stated to increase the adhesive power of the glue, preserves it from putrefaction, and forms a kind of mordant, acting as a binder between the paper, the casein glue and any added colouring matter.

Pure casein, free from ash, is obtained by precipitating 1,000 parts of cold milk with 2·9 parts of acetic acid which leaves the bulk of the lactalbumen in solution. The filtered and slightly washed precipitate is purified by repeated solution in water containing sufficient commercial ammonium carbonate to furnish a decidedly alkaline reaction, the filtered solution being then neutralised with acetic acid. According to Béchamp, one part of this pure casein dissolves in about 1,000 parts of water, as well as in alkalies and acids.

The Hoppe-Seyler method of preparing casein, as practised by Hammarsten, consists in treating milk with acetic acid, and dissolving the precipitate in the minimum quantity of dilute ammonia or sodium carbonate, an alkaline reaction being guarded against. This operation is repeated, the casein being then treated with alcohol and ether to completely eliminate the contained fat, a second treatment with acetic acid and soda completing the purification. Provided a strongly alkaline reaction is avoided, the casein is not decomposed. The removal of fat can be facilitated by employing skimmed milk in place of new milk.

According to another report, pure casein is obtainable by diluting milk with four times its own volume of water, and then adding sufficient acetic acid to bring the acid content of the mixture to 0·075-0·1 per cent. The precipitate is purified by trituration under water, and then immediately redissolved in very dilute potash, followed by reprecipitation with acetic acid. The casein is washed with water, rubbed down fine with 97 per cent. alcohol, drained and washed with ether.

Besana gives the following instructions for the preparation of casein for technical purposes:—

Skim milk from the separator is heated to about 95° F. in a cheese vat or similar vessel, direct steam being used if necessary. It is then treated with about 3 parts per mil. of crude hydrochloric acid, previously diluted with 5 to 6 volumes of water, whereby it is curdled, the whey being drained off and the curd spread out in a thin layer on a sloping table to cool. This done, the mass is washed with a spray of cold water or churned with water, which is drawn off after the curd has subsided. After removing a further quantity of water by pressing the curd in a weighted sack or in a press under moderate pressure, the product, which is still moist, is comminuted in a curd mill and is ready for sale in the damp state.

Casein, in the form of powder, is the kind usually required for technical purposes. Various forms of drying apparatus may be used, such as the hot-air apparatus for drying vegetables or heated drying chambers fitted with frames for supporting superimposed trays made of strong canvas, permeable to moisture. These hot-air appliances consume a considerable amount of fuel and are troublesome to manage unless fitted with expensive mechanical stirring or turning devices, the constant turning and breaking down of the casein being necessary. At the same time a constant drying temperature, between 122° and 175° F., must be maintained. For this purpose the following arrangement has proved very satisfactory and cheap, besides enabling the heat to be efficiently utilised. Two small brick walls, about a foot high, are built, without foundations, 40 inches apart, each being topped by a coping of wood 6 inches square. The coping is surmounted by a thick strip of damp millboard about 2 inches wide, and this in turn by plates of sheet iron, 40 inches by 80, and $\frac{1}{8}$ inch thick, fastened down by screws, so as to form a long horizontal flue 40 inches wide and 12 high. Where the ends of the iron plates join they are supported by wooden traverses to which they are screwed with an intervening layer of millboard as in the case of the copings. The two ends of this flue are closed by brick walls through one of which exhaust steam is introduced, whilst an opening in the other enables the steam to escape into a small chimney. The flue should have a gentle slope towards this end so that the condensed moisture may drain away. The casein may be dried very quickly on these iron plates by spreading it out on the farther end and turning it over with wooden shovels towards the hotter end. Unless erected indoors, the flue must be covered with a wide roof to protect the plates from rain. By means of this simple appliance, large quantities of casein can be dried in a short time, the only precaution necessary being to protect it from overheating by vigorous shovelling and breaking down the lumps, the flow of steam being also checked if found desirable.

By this means, 100 parts of skim milk will yield about 8½ parts of damp or 3½ parts of dry casein. This is put on the market as "technical casein" or "lactarin". It is soluble in alkalies but insoluble in water unless the latter receives an addition of 10 per cent. of some alkali (*e.g.*, soda, borax, or ammonia). The dry casein still contains about 10 per cent. of moisture, which constitutes one of the factors determining the quality of the product, though less important than the appearance and odour. The latter must on no account be ammoniacal, but should recall that of fresh milk, and the colour must be pure white. The purer the colour and the more agreeable the smell, the higher its value.

Soluble casein is obtained from the moist product by dissolving the same in an alkali (caustic potash or soda, ammonia, lime water, or baryta water), or in an alkali salt (carbonate of potash or soda), and evaporating the solution at a moderate temperature. This soluble casein is rarely prepared in dairies, since the industrial consumers of the article can make it more easily and cheaply themselves from the moist or dry product. On this account it is usual to specify the manner in which the moist casein is to be prepared. Consequently, when these particulars are specified in the contract, the casein-maker will do well to adhere to the instructions given, and not to employ some other method of preparation that may seem preferable to him, or he may conflict with the objects and views of his customer.

Another method of preparation, recommended by Just, is used in America, furnishing a light, dry, porous product. Although similar methods have been employed in Germany for some years, the inventor obtained a patent in that country, the specification of which reads as follows: "A process for preparing milk casein in a light, dry, porous form, consisting in distributing a dilute aqueous solution of casein in a uniform thin layer over a suitable surface previously heated to over 200° F., whereby the casein is dried, the operation being performed under ordinary atmospheric pressure". The following modification is also described in the specification, but is not protected by the patent: Twenty-five gallons of water heated to 105° to 110° F. and containing 1 to 1½ lb. of carbonate of soda in solution, are used to dissolve 175 lb. of moist casein or 119 lb. of dry casein, with continued stirring. Two metal cylinders, mounted so close together that nothing thicker than a strip of paper can pass between them, are rotated in opposite directions and heated by steam at a temperature of 212° to 220° F., the dissolved casein being allowed to flow between them. The liquid dries immediately, and the thin, brittle layer of dried material is scraped or brushed off the cylinders, whilst, if pressed through a hair sieve, it furnishes a fine, soluble casein powder.

This method is at all events cheap and simple, yielding a good, staple product, provided the fat and milk sugar have been properly eliminated. The granting of the German patent took two years, a sign of the tenacity with which the inventor fought his case, though such a claim as that set forth above is very little protection, as it is difficult to see where the novelty comes in.

According to a written communication from the inventor, the process has been worked in America on a large scale since March, 1903, one factory treating 260,000 lb. of skim milk daily, whilst a second factory began operations in October, 1903.

J. Ricard and C. E. Riche (French patent 364,635, March 27, 1906), dispense with any chemicals, stating that hydrated casein heated to 100° C. becomes sufficiently plastic to be rolled out into thin films, and is dried between two cylinders revolving in opposite directions or on one cylinder only, heated at 100°-110° C. The casein forms a thin film, which is removed by a scraper and can be readily pulverised.

Manufacture of Casein.—(H. V. Dunham, Bainbridge, New York; United States patent, 897,885, Sept. 8, 1908.) A process for producing a casein compound suitable for coating, which consists in curdling milk with commercial hydrofluoric acid diluted to such an extent that it has no appreciable corrosive action upon glass, and then separating the precipitated casein from the whey. A process of producing a casein compound suitable for coating, which consists in heating milk and mixing commercial hydrofluoric acid therewith, in the proportion of one pint to one quart of acid to one thousand quarts of milk and then separating the casein from the whey. A solution for sizing purposes consisting of approximately 94 per cent. of such casein, and 6 per cent. of borax, mixed with water.

Improvements in the Preparation of Casein.—(French patent 396,014: C. A. Baechler.) Milk, coagulated by means of rennet or an acid, is agitated in order to prevent the flakes of curd from agglomerating, and is at the same time treated with about one part per 1000 of a substance such as alum, which has a similar effect on the curd, the temperature being then raised to about 52° C. and stirring continued till the mass is cold. The resulting granular casein, which may be separated by a centrifugal machine, is neutral, but may be rendered alkaline by the addition of sodium bicarbonate, 3-5 per cent. of which (calculated on the dry weight of casein) will suffice to render the casein soluble in water. Acid casein may be prepared by treating the washed, neutral casein with a minimum quantity of acid; or an acid may be used to coagulate the milk.

In the patent granted to C. A. Baechler (English patent 6247, March 20, 1908), the effect of calcium salts in the precipitation of casein is made use of, skim milk at a temperature of 30° C. is mixed with a solution of calcium chloride in the proportion of about 0·5 part of the salt to 1,000 parts of milk, and then treated with a solution of rennet. As soon as coagulation commences the mass is well stirred to granulate the casein. One part of ammonia alum is next added and the casein separated and dried. The casein thus produced is in a finely divided condition, which obviates the necessity of drying. The casein in its moist state can also be treated with a suitable acid or alkali to produce acid—or alkali casein.

CHAPTER IV.

COMPOSITION AND PROPERTIES OF CASEIN.

CASEIN, the chief and characteristic albuminous substance in milk, was, on account of its acid properties, long regarded as an albuminate, and was classed along with the alkali albuminates obtained by denaturing other albuminous substances. Hoppe-Seyler, and more particularly Hammarsten, were the first to demonstrate its separate entity, its composition varying somewhat according to the animal from which it is derived.

The casein of cows' milk contains: Carbon, 52·96; Hydrogen, 7·04 to 7·53; Nitrogen, 15·60 to 15·91; Oxygen, 22·78; Sulphur, 0·758 to 0·82; Phosphorus, 0·8 to 0·847.

A. Burr[1] has examined a number of samples of casein, some of them of commercial origin, and others which he had himself prepared. The average composition of a number of samples of commercial casein was:—

Water	10·38
Dry substance	89·32
Fat	1·89
Casein	79·45
Ash	6·51

For caseins prepared by himself he obtained the following figures:—

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[1] "Milchwist. Zentralbl.," 1910, **6**, 385-394; "Jour. Soc. Chem. Indt.," 1910, 1327.

	4 Samples of Acid Casein.	4 Samples of Rennet Casein (Paracasein).	15 Samples of Curd, precipitated by Rennet and Acid.	Mean.
Water . . .	5·55-8·65	0·6-2·97	73·08-80·03	76·70
Dry substance	91·35-94·45	97·03-99·40	19·97-26·92	23·30
Fat . .	·005-·075	0·08-0·55	0·36-1·10	0·66
Ash . .	0·0	5·0-8·55	1·18-2·18	1·59

Nitrogen content of casein, fat and ash free .	15·58-15·63	15·64-15·74
Conversion factor	6·40-6·41	6·35-6·40

The elementary composition of casein is very similar to that of albumin and fibrin, as shown by the analyses of Mulder:—

ANALYSES BY MULDER.

	Casein.	Albumin.	Fibrin.
Carbon . .	53·83	53·5	52·7
Hydrogen . .	7·15	7·0	6·9
Nitrogen . .	15·65	15·5	15·4
Oxygen . .	23·37	22·0	23·5
Sulphur . .		1·6	1·2
Phosphorus . .		0·4	0·3
	100·00	100·0	100·0

The following are also analyses of casein by various observers:—

	Dumas.	Dumas and Cahors.	Jones.	Rochleder.	Scheerer.	Scheerer. By Alcohol.	Scheerer. By Souring.	Scheerer. By Acetic Acid.
Carbon . .	53·7	50·50	55·05	56·24	54·665	53·7	54·0	53·8
Hydrogen .	7·2	6·78	7·59	7·97	7·465	7·2	7·2	7·4
Nitrogen .	16·6	18·17	15·89	15·83	15·724	15·6	15·7	15·7
Oxygen . .	22·5	24·55	21·47	19·96	22·146	23·5	23·1	23·1
Sulphur . .								
Phosphorus .								
	100·0	100·00	100·00	100·00	100·000	100·0	100·0	100·0

Dumas and Cahors have examined the caseins derived from the milk of various animals, their results being given below:—

ANALYSES OF DUMAS AND CAHORS.

	Ppt. by Acetic Acid.			Ppt. by Alcohol.	
	From Cows' Milk.	From Goats' Milk.	From Asses' Milk.	From Sheeps' Milk.	From Human Milk.
Carbon . .	53·5	53·6	53·7	53·5	53·5
Hydrogen .	7·1	7·1	7·1	7·1	7·1
Nitrogen .	15·8	15·8	16·0	15·8	15·8
Oxygen, etc. .	23·6	23·5	23·2	23·6	23·6
	100·0	100·0	100·0	100·0	100·0

These samples were dried at 150° C. The ash varied between 1·5 and 5·4 per cent.

F. Tangl[1] has also made analyses of caseins from the milk of various animals, his results being as follows:—

	Milk of—					
	Cow.	Buffalo.	Sheep.	Goat.	Mare.	Ass.
Carbon .	52·69	52·88	52·92	52·90	52·36	52·57
Hydrogen .	6·81	7·81	7·05	6·86	7·09	7·01
Nitrogen .	15·65	15·78	15·71	15·48	16·44	16·28
Oxygen .	23·141	21·925	22·794	23·30	22·705	22·495
Sulphur .	0·832	0·833	0·717	0·70	0·528	0·588
Phosphorus .	0·877	0·773	0·809	0·76	0·877	1·057

H. Droop Richmond[2] found that the average percentage of nitrogen in casein estimated by the Kjeldahl process and calculated on the water and ash free basis is 15·65, which would give a conversion factor for the albuminoid of 6·39. The results obtained by the Dumas method are somewhat higher, which he ascribes to be due to the presence of unoxidised carbonic oxide in the combustion gases.

It is lacking in glycocoll and the carbohydrate group, but yields a large proportion of tyrosin and tryptophane. Accordingly, it is readily decomposed by pepsin and trypsin, it is also attacked by erepsin, but does not furnish any hetero-albumose on peptonisation.

Owing to the ease with which it is decomposed, casein also plays a special part in metabolism. The proportion of

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[1] "Pflüger's Arch. d. Physiol.," 1908, **121**, 534-549; "Jour. Soc. Chem. Indt.," 1908, 416.

[2] "Analyst," 1908, **33**, 179-184.

lysin and glutaminic acid is particularly high; and according to Wildenow and Salkowski, paranucleic acid contaminated with albumin containing 3 to 4 per cent. of phosphorus is also present. The salts of casein are specially important; and, though like all albuminoids, it is capable of forming compounds with acids, and is therefore readily soluble in an excess of acid, its own acid characteristics are demonstrable. It is therefore amphoteric in its reactions. According to Lacqueur and Sackur, the equivalent molecular weight of casein in its compounds with bases is 1,135, and its basicity is 4 to 6. In its acid functions, which are the stronger of the two, it is stated to behave as a tribasic acid; is also affirmed that it combines with a fixed amount of caustic soda, 1 gram uniting with 0·88 millimol. of NaHO to form a solution having a normal electrical conductivity but incapable of passing through a parchment membrane. The far higher molecular weights of 5,000 to 6,000, found by Salkowski, Hammarsten, Lehmann, Hempel and Soeldner, are based partly on hydrolysis and partly on the investigation of the acid salts. A. W. Bosworth and L. L. Van Slyke[1] estimate the molecular weight of casein at 8,888 and state that it contains two atoms of phosphorus. Söldner differentiates between two series of salts, Courant three. In milk, casein is supposed to be present as calcium caseate; and, according to Courant, not as the neutral salt, but as calcium dicaseate, combined with calcium phosphate. This point, however, is not yet conclusively decided. Revis and Payne also state that the casein is combined with calcium phosphate, while Richmond adduces evidence to prove that it is present as a calcium-sodium salt in combination with one molecule of calcium phosphate. Certain authorities believe that it exists as a lactate—calcium lactate—which is hardly probable.

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[1] See also p. 47.

Söldner[1] believes that the calcium in milk is present as mono- and di-calcium phosphate, which on boiling are converted into the insoluble triphosphate. According to Trunz,[2] milk contains approximately 0·18 per cent. of calcium, about 76 per cent. of this being combined with casein, the remaining 24 per cent. existing as phosphate and citrate. He found by experiment that of the total calcium present in the original milk 17·5 to 24 per cent. was precipitated on boiling, at the same time the percentage of phosphoric was found to be correspondingly decreased. Calcium caseate may, *per se*, possess the property of maintaining in solution or suspension the neutral calcium phosphate also present in the milk, or the milk may contain a true double salt of calcium caseate and calcium phosphate; in either case, the calcium phosphate is thrown down when casein is precipitated along with the total milk fat, the emulsification of which is therefore due to calcium caseate. This again is the reason of the great difficulty experienced in obtaining casein free from fat and calcium phosphate. According to Mulder casein contains about 6 per cent. of calcium phosphate. Whilst free casein is perfectly insoluble in water, the neutral sodium and ammonium salts are readily soluble. Even the acid salts of casein are soluble in water, but the solutions are strongly opalescent. Calcium caseate dissolves easily, but the solution has a distinctly milk-white appearance. Nutrose and plasmon are sodium caseate. Ammonium caseate is known as "Eucasein".

Casein is dissolved by solutions of alkalies, alkaline earths, carbonates, phosphates, borates, and other alkaline salts. Casein is precipitated from solutions of these salts, and therefore also from milk, by very weak mineral acids or by strong acetic acid, and is redissolved when the precipitating acid is

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[1] "Landw. Versuchs.," 1888, 351.

[2] "Zeits. f. physiol. Chem.," 1903-4, **40**, 263.

in excess. Casein adsorbs both acids and alkalies from solution, that is to say, when added to solutions of these substances they become more concentrated in the moist casein than in the unabsorbed liquid. This phenomenon of adsorption is common to colloidal substances, being due largely to their great surface energy, the material becoming condensed or concentrated upon the enormous surface which they exhibit. Together with this action is also to be noted the combination of a portion of the acid or alkali with the casein. Peculiarly both H and OH ions cause the swelling of casein at certain concentrations, the OH ions, however, having much the stronger effect.

According to Tangl[1] the adsorption of acids by casein is directly proportional to the acid concentration.

W. Van Dam[2] determined the amount of lactic acid adsorbed by casein from a $\frac{N}{20}$ solution at 18° C., using Bredig's ethyl diacetate method to determine the H ions left in the solution, and found that with quantities of casein ranging from 0·25 to 1 gram, there being an excess of H ions present, casein combined with a constant quantity of lactic acid which amounted to 4·25 per cent. of the casein present. With larger quantities of casein the proportion of lactic acid was relatively less. From his experiments he concludes that the molecule of casein contains four replaceable hydrogen atoms to one basic group.

J. H. Long[3] finds that at ordinary temperature combination of acids and casein takes place in the proportion of 1 gram of casein to 7 c.c. of $\frac{N}{10}$ hydrochloric acid, hydrobromic acid, hydriodic acid, sulphuric acid, or acetic acid,

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[1] "Chem. Zeit.," 1908, **1**, 1288.

[2] "Chem. Weekblad," 1910, **7**, 1013.

[3] "Jour. Amer. Chem. Soc.," 1907, **29**, 1334-1342.

also appreciable quantities of tartaric, phosphoric, oxalic, and other acids are similarly fixed. The affinity for bases is somewhat greater than this, 1 gram of casein combining with 9 c.c. of $\frac{N}{10}$ solutions of hydroxides or carbonates of sodium, potassium, lithim, or ammonium. On heating a larger proportion of acid is fixed owing to the hydrolysis which then takes place resulting in the formation of decomposition products which combine with acids.

L. L. Van Slyke and D. D. Van Slyke[1] have carried out a series of experiments to determine the action of very weak acids upon casein. The solutions employed by them were hydrochloric acid, sulphuric acid, lactic acid, and acetic acid in four different strengths, *viz.*, N/125, N/500, N/1000, and N/2000. The times of contact varied from five minutes to forty-eight hours and the temperatures were 0°, 25°, and 45° C. The effect of neutral salts, *e.g.*, potassium chloride and magnesium chloride on the course of the reactions was also studied. It was found that even after several hours contact at 0° C. little or no casein dissolved in acids not stronger than N/500, the same remark applies at 25° C. to solutions not stronger than N/1000. An increased solubility was, however, noted on raising the temperature, prolonging the time of contact or using acid of greater strength. The solvent action of the acids varied in the following order, hydrochloric, lactic, sulphuric, acetic, the first named being the strongest. The rate at which casein dissolves was found not to be directly due to the H ion concentration or to dissociation since the organic acids had a greater solvent power than would be accounted for if such were the case. The amount of acid taken up by the casein was determined by shaking the latter with the solution of acid and, after filtering, determining the loss in electrical conductivity of the solution which gave a

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[1] "New York Agri. Expt. Stat. Bull.," No. 3, 1906, 75-162.

measure of the amount of acid taken up. With 1 gram of casein and 100 c.c. of N/1000 hydrochloric acid, after three hours contact, 50 per cent. of the acid was taken up. The amount of acid adsorbed by the casein, however, varies with the concentration of the acid, the duration of contact, the temperature, and the nature of the acid. Some acid is removed even from the very weakest solutions, but the acid is never totally adsorbed even when the proportion of casein is relatively large. The amount of acid adsorbed when equilibrium was established varies practically directly with the concentration of the acid within the limits of the experiments (N/125 to N/1000), and the equilibrium ratio (that is the concentration of acid in 1 gram of casein divided by the concentration of acid in 1 c.c. of the surrounding liquid) is for sulphuric acid 675, hydrochloric acid 147, lactic acid 80, and acetic acid 30. The acid thus taken up is removed by continued washing with water. No adsorption of neutral salts, such as potassium chloride and magnesium sulphate was found to take place from dilute solutions. These results are in favour of the assumption that the reaction between casein and acids is an adsorption phenomenon, and the authors are of opinion that the souring of milk is due to the precipitation of free casein containing lactic acid held by adsorption.

In experiments on the titration of casein using different indicators it was found that the sodium salt readily hydrolyses and becomes alkaline so that it was impossible by this means to determine the molecular weight of casein. The acid character of casein being so very slight, it was also necessary to have a large excess of casein present in order to obtain an acid reaction with less sensitive indicators than phenol phthalein. Precipitation of casein or its salts ensues when the solution is saturated with common salt, magnesium sulphate or sodium sulphate. For the bulk of the casein the limits in the case of ammonium sulphate are 2·2 and 3·6, though a slight cloudiness is already observed when 1·2 is reached. In other respects casein behaves in acid, neutral or alkaline solution like the other albuminoids, *i.e.*, is precipitated by salts of the heavy metals $CuSO_4$, $ZnSO_4$, etc., and certain complex organic acids, so-called alkaloid reagents, when the acid is in excess also by tannin, metaphosphoric acid, and phosphotungstic acid. In addition, casein is thrown down by most acid aniline dye-stuffs and a few complex organic acids, but only when the reaction is decidedly acid.

Potassium alum, in suitable concentration, will throw down the casein in milk, without affecting the other albuminoids present. With an excess of the salt, however, the precipitate is redissolved. Other important compounds of casein are those formed when milk is coagulated by rennet, whereby the casein is transformed into paracasein. Like the unaltered casein, this substance is readily soluble in alkalies, though its calcium salt is insoluble; hence, when a soluble calcium salt is present in the liquid, insoluble calcium paracaseate or cheese is formed. The coagulation of milk proceeds in two stages, occurring successively, the actual enzymic conversion of the casein by the rennet ferment, and the visible coagulation for which alone the presence of lime is necessary. Paracasein is not precipitated when the soluble calcium salts of the milk have been removed by oxalic acid. Halliburton would confine the name paracasein to the coagulated casein, calling the soluble casein "caseinogen".

According to J. Mellanby,[1] caseinogen is obtained by mixing separated milk with three times its volume of alcohol and cooling to 15° C. The precipitate which forms is separated by filtration, digested with ether till free from fat, and then dried in the air at ordinary temperature. This

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[1] "Biochem. Jour.," 1915, 342; "Jour. Soc. Chem. Indt.," 1915, 1108.

material is a complex containing protein and calcium phosphate in the proportion of approximately 1 gramme molecule of calcium phosphate in 3,500 grammes of the material, which would suggest that one unit of protein weighing 3,400 grammes is combined with one molecule of calcium phosphate, the author expressing the formula as

$$CaXR . (NH_2)_2C_2H_2(PO_4)_2.$$

The group X having feeble acidic functions.

From a solution of caseinogen, six molecules of acetic acid precipitate acidic caseinogen or casein, of which 3,400 grammes contain 1 gramme atom of phosphorus.

L. Piet states that paracasein differs from casein by containing a higher amount of calcium and phosphorus, and after precipitation a greater amount of nitrogen and a smaller proportion of calcium are left in the milk serum or whey. Paracasein is also less soluble in a suspension of carbonate of lime in water, and is precipitated from its solution in lime water by phosphoric acid. According to the author casein contains 1·315 per cent. of phosphorus. In rennet casein he found 2·16 per cent. of calcium, and in acid casein 0·63 per cent.

In its other properties paracasein is identical with casein, but is thrown down more readily than the latter by common salt, so that it can be made to coagulate, by means of large quantities of salt without any addition of lime.

No real coagulation occurs when casein is exposed to high temperatures; and the solutions of its salts may be boiled without suffering any alteration. In the dry state, on the other hand, according to Lacqueur and Sackur, it becomes partly insoluble when heated to 94° to 100° C.; whereas, according to the earlier report by Hammarsten, this does not ensue below 120° to 130° C. Halliburton noticed a change when casein suspended in water was heated to 75° C. What happens to the casein when milk is boiled still remains unknown.

According to Richter, casein is precipitated from its solutions by sodium chloride, ammonium sulphate or magnesium sulphate without change, leaving albumin and nuclein in solution. Pure 2 per cent. solutions of casein and paracasein are, however, not salted out by a saturated solution of common salt according to S. Schmidt-Nielson.[1] On the addition of 0·4 per cent. of calcium and 0·05 per cent. of magnesium in the form of salts the casein is precipitated in the form of an alkaline-earth caseinate. For the complete precipitation casein requires 6·5 per cent. and paracasein about 3 per cent. of their weights of calcium respectively. Barium and mercury ions behave similarly, but are not so effective, being only about one-third as strong in their action. Mineral acids in excess precipitate casein solutions. The solutions of the alkali and calcium salts of casein do not coagulate on heating. A lime-free solution of casein is not coagulable by rennet, though it becomes so when a calcium salt is added, even though in the meantime the rennet has been rendered inactive by boiling.

After Hammarsten had investigated this action of calcium salts on the curdling of milk by rennet, S. Loevenhart demonstrated that a similar effect is produced by the salts of lithium, beryllium, magnesium, strontium and barium, as also by the proto-salts of iron, cobalt, nickel, and manganese.

Purified casein is a snow-white, perfectly ashless powder. A solution of casein shows a specific rotation of – 87° or in strong solution – 91°. The heat of combustion of 1 gramme of casein is 5·858 cal. It strongly reddens blue litmus paper, but is only soluble to the extent of a trace in water, though soluble in alkalies and in water containing calcium carbonate.

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[1] "Bietr. z. chem. Physiol. u. Pathol.," 1907, **9**, 311-321; "Jour. Soc. Chem. Indt.," 1907, 709.

It also dissolves in a 1 per cent. solution of sodium fluoride, and in ammonium oxalate or potassium oxalate. From solutions it is precipitated by acids and by rennet. In the presence of salts (sodium chloride, and especially sodium acetate) the precipitation by acids is incomplete. When purified milk casein is boiled for five hours with 3 parts of hydrochloric acid (specific gravity 1·19), tyrosin, leucin, leucinide, C_5H_7NO, a little aspartic acid and glutamic acid are formed.

Schutzenberger found that on heating casein with baryta water in a sealed tube to 150° C. it is split up into the elements of urea (CO_2 and NH_3), traces of sulphurous acid, sulphuretted hydrogen, oxalic and acetic acids, tyrosine, the amido-acids of the series $C_nH_{2n+1}NO_2$, corresponding to the fatty acids $C_nH_{2n}O_2$, from amido-oenanthylic acid to amido-propionic acid, leucine, butylamine $C_5H_{11}NO_2$, and amido-propionic acid $C_4H_9NO_2$ together with several other products either not well known or unidentified. Aberhalden has also determined quantitatively the products obtained by the hydrolysis of casein, but, as pointed out by J. B. Osborne and H. H. Guest,[1] the last named author was able to identify and determine only about 50 per cent. of these. They therefore undertook a re-examination of the question with the result that 67·85 per cent. was accounted for as follows: Glutamic acid 15·55, leucine 9·35, valine 7·2, proline 6·7, lysine 5·95, tyrosine 4·5, arginine 3·81, phenylalanine 3·2, histidine 2·5, tryptophane 1·5, aspartic acid 1·39, diamido-trihydroxydodecanic acid 0·75, serine 0·5, oxyproline 0·23, ammonia 1·61, phosphorus 0·85, sulphur 0·76. The residue, containing substances which could not be identified had a mean nitrogen content of 13·1 per cent.

In the treatment of casein for the preparation of waterproof coverings (paints, varnishes, etc.), and particularly of

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[1] "Jour. Biol. Chem.," 1911, **9**, 333-353.

plastic masses intended as substitutes for celluloid, or for other purposes, an important part is played by substances which precipitate the casein in an insoluble form from its solutions. Though this may preferably be done by heating solutions or mixtures of casein along with lime or milk of lime, still heat is not applicable in all cases. Such precipitation can be effected at the ordinary temperature by treating the casein solution or mixture with metallic salts, especially those of copper (cupric sulphate), or with certain organic substances, *e.g.*, alkaline solutions of shellac, the addition of which immediately separates the water contained in the mass. A patent for the production of insoluble casein was taken out in America by Dunham, according to which 15 parts of borax and 85 of commercial casein are dissolved in 400 parts of water, the solution being then treated with 15 parts of hexamethylene tetramine (produced by the action of ammonia on formaldehyde) and afterwards evaporated, the dried product being exposed to warmth and moisture. In this form casein is a suitable substitute for albumen for certain purposes.

A far more important matter to the casein industry is the German patent 99,509, or rather the addition to that patent, according to which casein, albumoses, and the liquid conversion products of glue and gelatine are rendered insoluble by formaldehyde. The insoluble products thus obtained can and do find technical application in the form of layers or coatings, as detailed below.

For certain purposes in chromo-lithography it is necessary to provide paper with a perfectly smooth, absorbent and yet resistant surface. This object is now accomplished by coating the paper with size or casein hardened with formaldehyde, a simple operation which has become of great importance in the paper industry as well as in chromo-lithography.

Similar fine, insoluble layers of casein can also be prepared without a paper backing, and are then specially adapted for supporting sensitised emulsions in photography (photographic films). In this case they supersede the celluloid hitherto used, being free from its objectionable qualities, inflammability and so forth.

Coatings of casein may also be applied to wall paper, improving its durability and making it washable.

It is, however, neither essential nor desirable that this coating should be applied when the paper is being made, since the continuity of the coating would, in that case, suffer when the paper was being cut and hung. It is therefore preferable to apply the coating when the paper is on the walls; and experience has shown that this can be done with ease and perfect success.

A solution of casein and formaldehyde is also suitable as a coating for smooth brickwork, in all cases where a waterproof and washable coating is desired. The varnish paints and enamel paints now used for this purpose are more troublesome, dearer, and have the great drawback of continuing to smell for a long time. On the other hand, casein varnish is cheap, easily applied, loses all smell in a few hours, and also forms an excellent disinfectant. This is certainly a valuable property for hospitals, barracks, dormitories, rooms, etc.

The insoluble compound of casein and formaldehyde can also be obtained in large blocks; and by means of a patent process, owned by the Vereinigte Gummiwaaren Fabriken Harburg-Wien (formerly Menier & Reithoffer), it is prepared in solid, horny plates and bars, forming a perfect substitute for ivory, ebony, horn, tortoiseshell, celluloid, coral, etc. The inventor has applied the name "galalith" to this product.

The properties of galalith are such as to ensure for it a great future. It is inodorous and uninflammable, thus possessing, as already mentioned, a great advantage over celluloid. It can be dyed, and the crude article can be bent, blocked, and stamped while warm, retaining its form perfectly when cooled. It does not attack metals, and is one of the best insulating materials known for electrical purposes. These qualities are sufficient to secure for galalith a very extensive sphere of application, certain to react favourably on the milk industry.

Already this material is used for manufacturing a large number of articles, such as plates, combs, cigar-holders, household fittings, etc.; and it is also possible to utilise galalith for accomplishing new technical results.

When a solution of casein is treated with formaldehyde and poured on to glass plates it furnishes transparent films, which are insoluble in water. Spitteler and Krische found that the addition of formaldehyde to casein solutions gave, on subsequent precipitation, products that swelled up in water and had a fracture like cartilage. On the other hand, they discovered that this drawback could be remedied by treating the casein with formaldehyde after precipitation by acids or lead acetate, preferably after the precipitate had been freed from water, as far as possible, by evaporation or pressure, the hardening with formaldehyde being then undertaken. This treatment yields products with the properties of horn. In their patent specification the inventors give a comparative table of the behaviour of buffalo horn and of casein products prepared in various ways, showing that while buffalo horn absorbs 15½ to 18 per cent. of water, when submerged in that liquid for thirty-three days, the new product hardened with formaldehyde takes up 16 to 23 per cent. of water, behaving, therefore, in a very similar manner.

The *estimation of casein* is performed by precipitating the milk by saturation with magnesium sulphate, the nitrogen in the precipitate being determined, and the casein calculated from the result. The filtrate from the casein precipitate is diluted, and the lactalbumen thrown down with tannic acid or phospho-tungstic acid, the nitrogen in this precipitate being also estimated.

Analysis of Industrial Casein.—A good industrial casein should be properly and carefully prepared by souring fresh milk and washing and drying the curd so that no extraneous solids are present. The odour should be fresh, and not mouldy or rancid. On being treated with ammonia and left to stand for several hours, the sample should not leave any undissolved sediment, but should furnish a clear syrupy solution. Moisture content.—5 grammes of the sample are weighed into a nickel capsule and dried at 100° to 105° C. until of constant weight. Overheating causes error due to oxidation. Fat content.—A weighed quantity of the sample is extracted with alcohol and ether in a Soxhlet apparatus, the solvent being then expelled and the extract weighed. Ash.—2 to 3 grammes of the finely powdered sample are weighed into a quartz capsule, carefully incinerated and washed with water, the residue being moistened with ammonium nitrate, calcined at white heat, the solution in water added, evaporated and dried at 100° C., and weighed. Acid casein is harder to incinerate than that made with rennet, and contains less ash, the maximum being 6 per cent. as compared with up to 8½ per cent. Free acid.—10 grammes of casein are shaken up with 100 c.c. of water and filtered, 60 c.c. of the filtrate being treated with a few drops of phenolphthalein and titrated with decinormal potash until tinged with red. Well-made casein should only contain a very small amount of acid, especially when it has been in store for some time. The test is best applied in comparison with a sample of known purity. Solubility.—This is a particularly important determination, since it enables the presence of accidental or intentional additions of sand to be detected, and old casein to be distinguished from fresh. The test is performed by weighing 10 grammes of air-dry substance into a test glass and leaving it in contact with 50 c.c. of water and 1 to 2 of 33 per cent. ammonia for several hours, heating to 60° C. if the casein does not dissolve without. If pure, the substance will swell up and furnish a transparent, syrupy solution. Casein which has been stored for a long time or dried at too high a temperature gives a cloudy solution. Sand and other impurities are deposited as sediment. To ascertain their percentage, 1 gramme of the sample is dissolved in 25 c.c. of water and 10 drops of ammonia, the sediment being decanted, boiled with hydrochloric acid to separate the sand from organic impurities, starch, etc., and collected on a weighed filter, incinerated, and weighed. Organic impurities are detected by the microscope. The solubility in borax is tested by adding powdered borax to the casein mixed with water, and noting the amount needed to effect complete solution.—" Rev. Prod. Chim."

CHAPTER V.

CASEIN PAINTS.

THOUGH it has long been known that casein combines with certain substances to form agglutinant compounds, which become more or less insoluble on exposure to the air, and though it has been stated that casein has been detected in old paintings, nevertheless it is only within the past forty to fifty years that any extensive use has been made of it for this purpose. That an addition of milk to lime-washes greatly increases their durability has also long been known; and, in fact, such a mixture constituted the first casein paint, the caesin of the milk forming with the caustic lime a compound which is the basis of all such paints. The casein is rendered soluble, a result that can be produced, not merely with quicklime, but also with various substances having an alkaline reaction. The chief casein paints we shall here consider are those met with in commerce in the paste or liquid form, containing the casein in a disseminated condition, and in some cases already mixed with other substances used in paint, such as linseed oil, boiled oil, resins, or petroleum, in order to produce special effects. Others again—and of late these have become the more important—are supplied by the makers in the form of powder, and contain casein and alkali in the dry state. It is only when these paints are mixed with water, to render them fluid for use, that the alkali is dissolved, and, in turn, acts as a solvent for the casein.

The coatings furnished by the different kinds of casein paint dry with a matt surface, *i.e.*, without gloss, like all water-colour paints, and therefore exhibit a property which is difficult to impart to oil paints without impairing their durability. Under the influence of the air, the paint also acquires a certain firmness, and does not rub off like lime-washes. It is fairly durable when exposed to the air, but when placed in situations where it is exposed to wet or heavy rains, *i.e.*, on the weather side of a building, it suffers more quickly than oil paints. On the other hand, all casein paints have the advantage of drying quickly and being easy to work, without requiring any special preparation of the surface to be painted, drying without gloss, on brickwork, plaster, wood, canvas, etc., and without stopping the pores of brickwork. These paints are soaked in cold water in order to dissolve the soluble binding constituents, salts and similar compounds, so that they may dissolve the casein completely when diluted further with water, and also perform their chemical functions. In addition to the binding constituents the paint powders of this kind contain mineral matters (whiting, china-clay, clay, caustic lime, etc.), which form the bulk of the mass and give covering power, whilst body colours are also present to produce the desired tint. The pigments, which are added in merely minute proportion in the case of pale tints, must be perfectly unaltered by lime and alkalies. Consequently, a green, for instance, compounded of Prussian blue and chrome yellow, could not be used; the pigments used must be as pure as possible.

The media of these cold-water paints, and on which their quality and utility chiefly depend, are mostly albuminous substances of vegetable or animal origin, generally casein, dissolved by means of alkalies and afterwards rendered insoluble by the action of air on the coat of paint, as already stated. Excellent paints are also made from blood albumen and similar substances; but in some cases, glue, mucilage, dextrin, glutin, or starch, in admixture with certain salts, are also employed, insoluble compounds being thereby formed.

The paints with a basis of casein have proved to be the best, and are most extensively used. They are made from commercial casein powder, which readily dissolves in suitable proportions of caustic lime, ammonia, or alkaline salts. When blood or blood albumen is used, the one must first be well dried and the other finely ground, in order that they may form a good bind with caustic lime. Glue also must be ground, and the mass may be treated with potassium bichromate, tannin, alum, etc., to render it insoluble. Glutin must be allowed to ferment, and then be dried, ground and mixed with a certain proportion of alkali for use.

In preparing all these powdered paints, which are to be made up into a wash with cold or hot water or milk of lime, the main point is to adjust the proportions of casein, starch, glue, glutin, or other albuminoids so as to properly fix the pigment used for covering purposes and also for producing the tints. An insufficient quantity of the medium would lower the durability of the paint below the useful limit, so that it would not stand the action of rain, snow, etc., and would wipe off with the hand, or a brush.

On the other hand, an excess of medium would make the paint streaky and liable to crack and peel off. Since the loading materials used require very different quantities of binding constituents to fix them properly, this circumstance must be borne in mind. The same applies to the body colours, which require a larger or smaller quantity of binding ingredients, according to whether they are specifically heavier or lighter. These pigments should be able to retain their colour when used in mixtures containing caustic lime alkalies, or substances with an alkaline reaction. Intimate admixture of the various ingredients is an important factor in these paint powders. The percentage of medium in the mixtures is relatively small, and yet it must be distributed in a perfectly uniform manner throughout the mass; otherwise, if one portion of the paint contained too much, and another too little, the result would be noticeable in the uneven character of the coat of paint after application. Careful mixing is therefore an essential feature.

To secure this result, the medium and pigments are placed in a sifting mill of the type shown in Fig. 12, made by Wm. Gardner & Sons, Gloucester. This consists of a mixing chamber surmounted by a hopper and a chamber, containing a spiral roller brush fitted and working exactly in a semi-cylindrical sieve. The materials are fed in at the top, and are carried round by the brush, all soft lumps being broken up until they pass through the sieve along with the fine powder. On the other hand, all the hard lumps and

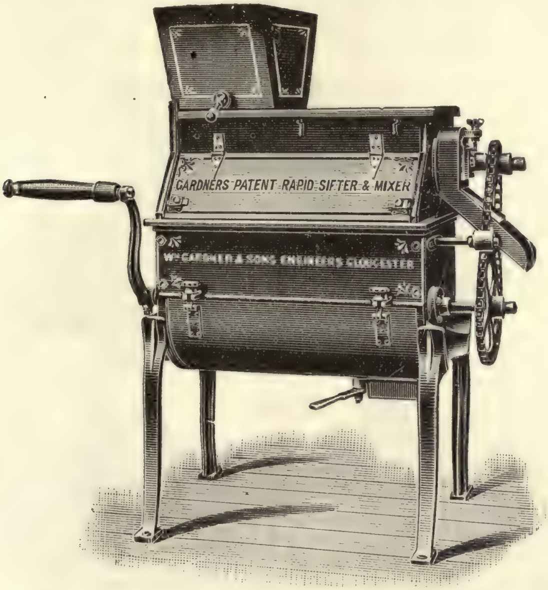

FIG. 12.—Gardner's "Rapid" Sifter and Mixer.

waste matters are discharged through an opening at the end of the machine. From 1 to 30 cwt. per hour can be sifted and mixed in this way, according to the size of the machine. Or after the ingredients have been carefully sifted they are put through a mixer of the Werner and Pfleiderer "Universal" type (Fig. 13). As, in these cold-water paints, powders of different densities have to be mixed together, the machine should be fitted with a two-speed gear—fast and slow. The fast speed acts as a sort of disintegrator, breaking up lumps and large granules thereby ensuring a more thorough admixture of the ingredients. Consequently, with a machine of this kind, the preliminary sifting may sometimes be omitted.

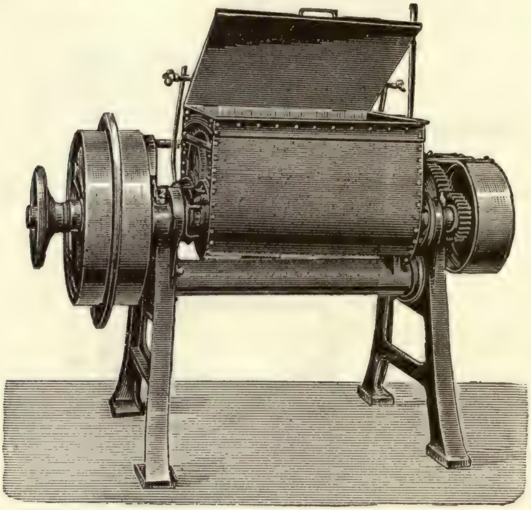

Fig. 13.—"Universal" Two-speed Mixer.

The product obtained by this process of fine sifting and intimate mixing will satisfy all requirements.

"Marble Lime" Colour for Outside Work.

The following ingredients are passed through a colour sifting and mixing machine:—

Casein, soluble in alkali	100 parts by weight.
Caustic lime from marble	100 ,, ,,
Levigated chalk (whiting)	800 ,, ,,
Borax	1 part ,,
Ultramarine (for white only)	2 to 2½ parts ,,

It is extremely important that the materials should all be very finely powdered. The caustic lime, $Ca(OH)_2$, is obtained as a fine white powder by slaking lumps of pure calcined marble lime with one-third their own weight of water in a porcelain vessel. The water and lime combine to form calcium hydrate, with liberation of heat and a faint alkaline smell. The resulting slaked lime should be kept in tightly closed vessels or, preferably, used immediately.

With regard to making this preparation in different colours, it should be noted that the mixing of the earthy pigments or so-called lime-proof colours may take place either when the paint is being made or else just before use (see instructions later). The following pigments are fast to lime: Antimony yellow, barium yellow, barium white, ivory black, chrome green (true), chrome orange, colcothar, green earth, cadmium yellow, cobalt blue, cobalt green, Mars brown, Naples yellow, ochre, Paris black, satinober, Schweinfurt green, Terra di Siena, ultramarine, umber, Vandyke brown, and zinc white. If the pigments are added at the time of manufacture, the weight of levigated chalk must be reduced in proportion to the amount of pigment used. For instance:—

Casein, soluble in alkali	10 parts.
Caustic lime	10 ,,
Levigated chalk	40 ,,
Ochre	40 ,,

Borax as before; ultramarine nil.

When, by making a little of the mass up into paint, the ingredients have been found to be thoroughly mixed, the powder must be packed in tightly closed boxes, lined with paper. In this way the article will keep indefinitely, in a dry place, without losing any of its properties.

The making of this powder up into paint is a comparatively easy matter, though a certain amount of care is necessary to ensure good results. The operation may be performed in any vessel that is clean and free from grease, in the following manner: 50 parts of water are added by degrees to 100 parts of the powder, with constant stirring, which is continued until the mass is homogeneous and free from lumps. The mass is then covered with a thin layer of water and left for about three-quarters of an hour, after which it is again stirred, and more and more water is added until a workable paint is obtained, of about the same consistency as oil paint. When intended for coating rough surfaces the paint should be a little thinner, but may be thicker when used to replace oil paint for smooth surfaces. It should be used without delay, as it is liable to set hard in a comparatively short time, becoming unfit for use in about twelve hours.

Hence it is not advisable to make up any more of the paint than can be used the same day. If, after the paint has remained some time in the vessel, it skins over, this skin must be removed before again using. Made-up white paint of this kind can be afterwards coloured by mixing up the pigments with water to a semi-fluid mass, and stirring this into the paint until uniformly incorporated therewith. In this case also it is desirable to try a little of the paint before using it on the work in hand.

The application of the paint and the preparation of the surface are carried out in the same way as mentioned in the chapter on casein painting. A solid and clean surface is essential to success. As the paint will adhere to any solid surface, such as lime, plaster of Paris, or cement, plaster, brick, metal, stone, or wood, as well as canvas without any preparation, all that is necessary is to clean the surface of dust and dirt. Painting can then be begun at once. The paint is laid on with a clean, but somewhat worn brush, free from grease, the paint working better than with a new brush. It is laid on fairly thick and spread by working the brush about, this method ensuring a better hold on the substratum and giving a more uniform coating free from spottiness. In other respects the operation is much the same as when oil paint is used; and the paint itself is stirred in the can at frequent intervals.

The paint dries very quickly, as smooth as enamel, and in thirty-six to forty-eight hours can be washed and will stand the weather. On account of its elasticity it can be varnished, painted or stencilled on. If applied to a firm substratum, it will neither crack nor peel off; but the surface must be freed from old coatings of lime-wash or distemper before the casein paint is laid on. In the case of oil paint that is still intact, this precaution is not necessary.

If it is desired to have a glossy paint for indoor use, the painted surface is sprayed over with a liquid mixture of wax and turpentine, which is afterwards polished.

Notwithstanding their power of standing weather, cold-water paints are porous and do not prevent the circulation of air. On account of their good qualities, these paints are in frequent use both for outdoor use and for interior work, in dwelling-houses, factories, hospitals, etc., as also for coating wood, iron, cement, etc.

Casein Paint according to an Older Method.—The curd of sour milk is boiled for about a quarter of an hour in an enamelled or glazed vessel and then transferred to a sieve, where it is washed with cold, hard water until perfectly free from acidity, after which it is wrapped in a cloth and pressed until only a little moisture is left. In this condition it is mixed with one-fourth of its weight of burnt lime, previously slaked with a threefold weight of water, the colouring matter, mixed or ground with oil or water, being next added. The resulting paint may be applied to stone, gypsum, or zinc, but if intended for use on wood it should be first mixed with 10 per cent. of linseed oil. If too thick, the paint can be thinned with oil or water.

SUNDRY RECIPES FOR CASEIN PAINT.

Casein	144 parts by weight.
Slaked lime	7 ,,
Spanish white	280 ,,
Earth pigment	2 ,,
Water	160 ,,

Another proved recipe is :—

Skim milk	½ gall.
Freshly slaked lime	6 oz.
Linseed oil or poppy oil	4 ,,
Spanish white	3¾ lb.

The analysis of a casein paint for coarse work showed it to have the following composition : Dry residue, 51·6 per cent. ; water, 48·4 per cent. ; ash in residue, 29·7 per cent. ; nitrogen, 0·537 per cent. ; (= to casein, 3·36 per cent.). The ash consisted of 24·6 per cent. of calcium oxide, 3·1 per cent. of silica, and 2·0 per cent. of ferric oxide. The silica was derived from the earthy pigment used. This paint can be imitated by slaking 30 parts of quicklime with 70 parts of water, allowing the product to cool, and then stirring into it 20 parts of white curd obtained from separated milk. A suitable amount of pigment is added to the mixture.

In the manufacture of liquid casein paints it is essential for good work to have the materials thoroughly ground together, for which purpose the dry pigments should be mixed with a portion of the casein solution sufficient to make it into a thick cream. This liquid is then passed through a cone-paint mill of the type shown at Fig. 14, by

Messrs. Follows & Bate, Ltd. The material, after passing through such a mill, will be found to have become much stiffer in consistency and finer in texture. It will also be found that on diluting with more of the liquid the pigment will remain suspended for a much longer time than before the grinding.

Casein Enamel Paint.—To prepare casein enamel paint, soda casein is intimately mixed with enamel colours—namely, glass fluxes coloured with metallic oxides (like the preparations used in porcelain painting), the whole being ground in water. The product on drying has not the dull surface of the ordinary casein paints, but shows a gloss more nearly resembling that of oil paint.

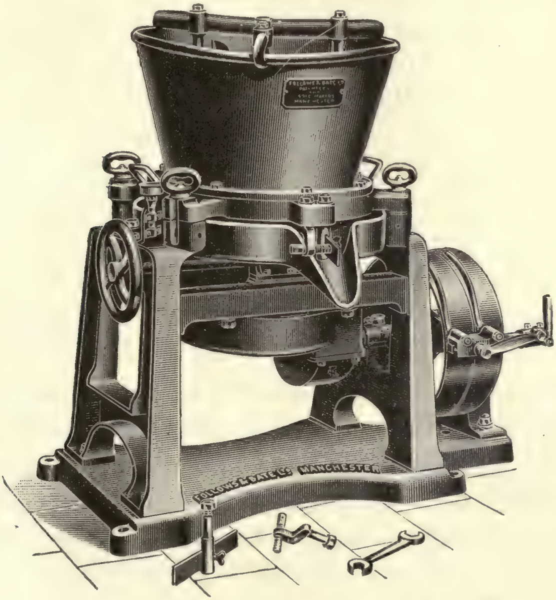

FIG. 14.—Cone Paint Mill. Follows & Bate, Ltd.

Casein Façade Paint.—This is a new type of ready-made casein paint, the chief peculiarity of which is that it must be protected from contact with carbonic acid gas before use, and therefore needs to be packed in airtight tins. These paints can be made in a variety of colours, and in the form of a thick cream, which is diluted with water for use. They are prepared by intimately mixing 200 parts by weight of casein in a pulverising machine with 40 parts by weight of powdered and sifted slaked lime, the whole being stirred to a thick fluid with a body colour that has been mixed with water. Finally, the paint is put through a paint mill and packed in airtight tins.

The most suitable pigments for this purpose are :—

For White.—Zinc-white, lithopone, blanc fixe, barytes.
,, *Yellow.*—Ochre, Indian yellow, Naples yellow.
,, *Brown.*—Umber.
,, *Black.*—Ivory black, vine black, lampblack.
,, *Red.*—Red lead, colcothar, Indian red, madder red.
,, *Blue.*—Ultramarine, cobalt blue, smalt.
,, *Green.*—Green earth, cobalt green, chromic oxide green, etc.

Cold-water Paint in Powder Form.—In making this class of paint the proportions must be adjusted in such a manner that the mixture shall contain 80 parts of dry casein to every 2½ parts of dry slaked lime (or caustic soda or potash). Useful results can be obtained from the following recipes :—

Powdered casein	45	parts by weight.
,, slaked lime	20	,,
Kaolin	150	,,
Levigated chalk (whiting)	300	,,
Pigment, according to the colour desired	5 to 20	,,

For a stone-coloured paint, the following proportions are suitable :—

Above paint mass	100	parts.
Light or dark French ochre	3	,,
Chrome yellow	2	,,
Cassel brown	1½	,,

or any of the pigments mentioned below, together or separately, may be used :—

Colcothar	1½ parts.
Vine black	1½ ,,
Graphite	2 ,,
Chrome green (limeproof)	4 ,,
Stone green	4 ,,
Ultramarine	2 ,,

Casein-lime Colours.—Casein is an important material for tempera painting, and the use of casein-lime colours for ordinary painting has been long known. In consequence of the high price of linseed oil, casein-lime colours are being much more generally employed, and great pains have been taken in improving this material to fit it for use as a substitute for ordinary oil colours. If this object has not yet been fully realised, none the less, casein-lime colours are now well established, and are being much more frequently used as better methods of application are discovered. It is very important in dealing with any kind of paint, to know exactly how it should be applied. When casein-lime colours were first put upon the market much disappointment was caused by unsuitable methods of application, which resulted in a strong prejudice against them.

These colours cannot be recommended for every purpose, and certainly not as a substitute for oil colours. However, if prepared from suitable raw materials and applied in a proper manner, they are perfectly satisfactory for certain classes of work. The successful use of these colours depends upon the formation of a casein-lime compound produced by the two components, casein and slaked lime, in the presence of water. The casein-lime binds the other mediums together. It is, of course, necessary to choose materials which are not easily affected by physical influences, and especially by atmospheric conditions.

Tempera colour contains about 85 per cent. of finest prepared chalk, with about 10 per cent. of casein and 5 per cent. of calcium hydroxide. Casein used for tempera colours should always be of the finest quality, pure white in appearance, the finest powder, and quite free from any suspicion of decomposition. Inferior brands sometimes contain decomposition products formed by over-drying the casein. These are not fit for tempera colours, notwithstanding their low price. They do not possess sufficient binding power, and very often the decomposition of the matter referred to causes streaks of yellowish colour on the painted surface. These substances also sometimes contain soluble salts which are dissolved more or less by rain, resulting in bad colours in outside work.

The properties of the calcium hydroxide used for tempera colours are also important. It should always be in the form of very fine powder, and, if possible, be freshly made; in no case can it be kept in stock for any considerable period of time, as it takes up carbonic acid from the air. The calcium hydroxide should therefore be prepared on the spot. Freshly burned white lime entirely free from iron, if possible, should be treated with exactly the quantity of water which it will take up; an excess of water must be avoided, and great care must be taken to prevent the formation of lumps; the fine powder thus obtained should be machine-sifted and then stored in airtight drums or casks. The lime should not be slaked with water in the open air, but the operation should be carried out in drums; a very fine powdered calcium hydroxide is thus obtained, which can be passed on to the sifting machines in enclosed trucks.

It is highly important that the chalk for casein-lime colours should be perfectly dry; if it contains any trace of water this causes lumps in the product, owing to the imperfect formation of the casein-lime compound, and these lumps are not broken up when the colour is mixed with water. On account of the price, a good natural chalk must be chosen, the covering power of which must be thoroughly tested. Sometimes the natural product, although sufficiently white, is of a crystalline structure, and, therefore, poor in covering power. This could be remedied by an admixture with a certain amount of artificially precipitated carbonate of calcium. Artificial chalk is quite amorphous, and therefore has a better binding and covering power than the natural product; the price of tempera colour permits its use in moderate quantities. Sometimes the superior kinds of china clay are mixed with chalk to be used for casein-lime colours. An excess of china clay must not be used if a good article is required; the use of china clay, it is believed, causes the colour to crack more readily under the influence of the atmosphere. The pure white casein-lime colour can be obtained only by using chalk alone. A yellowish tint is sometimes caused by the presence of minute quantities of iron in the chalk or hydroxide of lime. This can be remedied by adding ultramarine. If other shades are required, the chalk is mixed with certain quantities of earth colours fast to lime. Heavy pigments such as white lead, and, of course, all pigments which are not fast to lime, must be avoided. Good earth colours, such as ochre (hydrated oxide of iron), are most suitable, and can be used in considerable proportion, up to 30 per cent. or more.

The pigments must, of course, be mixed in a perfectly dry state. If the casein-lime colour is required for interior work, pigments only can be employed. Sometimes boric acid or other antiseptics are mixed with the colour for sanitary purposes, 1 per cent. being the usual proportion. It has been found best to mix the casein with the chalk and the pigment colours first, and then to add the hydroxide of lime. This method retards the action of the two vehicles. The colours when ready are stored and despatched in airproof receptacles to prevent any binding of the lime and casein. Casein-lime colours do not hold well on wood or metal; the coat very soon shows a tendency to become detached from the ground, as iron and wood are readily influenced by temperature; on the other hand, these colours are very suitable for stone surfaces and especially for freshly prepared cement walls. The surface to be painted and the painting material being of the same chemical nature, the result of the cohesion is very good.

Casein-lime colours cannot be recommended for painting over surfaces already covered with old lime or oil paint. Thorough examination of the surface to be painted should be made before casein-lime colours are applied. The colour should first be mixed with a little water, equal to about half the weight of the dry colour; the pulp thus obtained should be allowed to stand for a quarter or half an hour, and then about twenty or twenty-five parts more of water should be added and stirred in. The painting material is then ready for use. If a glossy coat is desired, only about ten parts of water are used in the second application; the ready-made pulp is then thick and more like an oil colour in appearance. If well made from suitable materials and carefully applied, casein-lime colours give excellent results and are found to be thoroughly satisfactory. The success of the casein-lime colour depends on its suitable application, and rests upon a thorough knowledge of the character of the paint in question and its behaviour with the surface to be painted.

Kistory's Recipe for Casein Paint and Varnish.—Professor Modets Kistory, of Moscow, recommends for casein varnish a mixture of 32 parts of sifted curd and 32 of water, stirred together at 64° F., the pulp being forced through a metal sieve in order to secure the subdivision of the particles and their more intimate admixture. Meanwhile, some freshly burned lime is gradually slaked with water at the above-named temperature, so that it crumbles down to a fine dry powder. Of this powder 1½ parts are mixed with 7½ parts of water, triturated, and then filtered through blotting-paper. The two ingredients are finally mixed together by stirring, which is continued until the mass, originally somewhat stiff, has attained workable consistency.

Pure Casein Paints for Walls, etc.

1. *Black.*

Casein varnish	50 parts by weight.
Lampblack	13 „ „

2. *Yellow.*

Casein varnish	50 parts.
Chrome yellow	10 „

3. *Chalk White.*

Casein varnish	50 parts.
Chalk	32 „

4. *Fine White.*

Casein varnish	50 parts.
White lead	35 „

5. *Red.*

Casein varnish	50 parts.
Vermilion	16 „

6. *Cheap Red.*

Casein varnish	50 parts.
Colcothar	60 „

7. *Blue.*

Casein varnish	50 parts.
Berlin blue	8 „
White lead	4 „

8. *Green.*

Casein varnish	50 parts.
White lead	14 „
Chrome green	21 „

9. *Ochre.*

Casein varnish	50 parts.
Ochre	12 „

Casein Paints for Woodwork and Iron.

1. *Black.*

Casein varnish	50 parts.
Black, ground in oil	15 „

2. *Yellow.*

Casein varnish	50 parts.
Chrome yellow, ground in oil	25 „

3. *Chalk White.*

Casein varnish	50 parts.
Chalk, ground in oil	30 „

4. *White Lead.*

Casein varnish	50 parts.
White lead, ground in oil	50 „

5. *Red.*

Casein varnish . .	50 parts.
Vermilion, ground in oil .	50 ,,

or—

Casein varnish . .	100 parts.
Colcothar, ground in oil .	50 ,,

6. *Blue.*

Casein varnish . .	50 parts.
Berlin blue, ground in oil	40 ,,

7. *Green.*

Casein varnish . .	50 parts.
Chrome green, ground in oil	50 ,,

8. *Ochre.*

Casein varnish . .	110 parts.
Ochre, ground in oil .	50 ,,

Casein paints, drying without gloss, are therefore suitable for painting house fronts, iron and other metal work, and also for canvas. Their most advantageous application is for the purpose first named, since they can then be prepared in large quantity, used up at once, and will dry in a few hours. They enter into combination with the underlying plaster and are thereby rendered more durable.

The paints prepared as above are thinned to a workable consistency with further quantities of casein varnish, and are then laid on as evenly as possible, in the same way as oil paint. The first coating will dry in about an hour, and a second coating can be applied a few hours later. This property of drying quickly is a great point of superiority over oil paint, since casein paints can, therefore, be used during unfavourable weather and seasons without any fear of the paint washing away or peeling off. These paints are also inodorous, whereas the smell of varnish and turps clings to oil paint for a long time.

For woodwork the paint is prepared in the same way, but three or four coatings are necessary to cover the wood properly. It can then be grained and varnished, just as in the case of oil paint.

Ironwork must be coated with casein oil paint, as the ordinary casein paint will not adhere to the metal. The iron should be freed from rust and the paint applied in a thin coating. Owing to the rapid drying of the paint it is less subject to injurious influences, but should be protected from these as much as possible to prevent the paint washing or peeling off and thus defeating the object of the application.

Casein Distemper Paints.—During late years there has been a considerable development in the use of distemper paints, which are sent out by many makers under a variety of fancy proprietary names in the form of powders or paste, which only require thinning out with water to make them suitable for use, many of these being characterised by the fact that they will withstand a reasonable amount of washing or rubbing. Distemper painting, or the use of various pigments mixed with water, has long been practised; but applied in this simple way, the pigments were loose and rubbed off badly, therefore to fix them on the surface it has long been customary to add size or glue. But the development of the dairy industry, and the desire to utilise all the constituents of milk, has led to the production of casein in considerable quantities, its employment as a fixing agent to distemper paints being the consequent result.

Water-Colour Paints.—For indoor use: 100 parts by weight of casein are mixed with 15 parts of 90° to 92° Tw. soda solution and 885 parts of kaolin, chalk, or other white pigment. For outdoor use: 90 parts of casein are mixed with 40 parts of powdered slaked lime, 7½ parts of silica, and 865 parts of kaolin, chalk, or other white material.

Casein-Silicate Paints.—Casein-silicate paint is a mixture of casein with potassium or sodium silicate ("water-glass"), the casein being dissolved in caustic soda or potash and stirred up with the alkali silicate and a sufficient quantity of diatomaceous earth until the resulting grey-brown mass is perfectly homogeneous. The paint can be tinted by the addition of lime-proof colours up to 10 per cent. It forms a useful indoor and outdoor coating for stone, brick, and fresh dry plaster (lime or cement), and it can also be very advantageously used in very damp rooms. Cheap fireproof paints for wood, canvas, etc., can easily be made by mixing these silicate paints with asbestos or other fireproof material.

The addition of casein to water-glass causes a gradual solidification, so that, unlike ordinary silicate paints, the coating is not completely hard in a few hours, but only at the end of two to three days. This circumstance is owing to the formation of a compound between the casein and the alkali of the water-glass and the separation of colloidal silica and casein. If the paint is desired to possess greater elasticity it is advisable to add a small quantity of saponified water-glass along with the ordinary silicate solution; while a higher gloss may be obtained by adding a solution of shellac and water-glass.

Though silicate paints offer many advantages over oil paints they have failed to make much headway up to the present, owing to the difficulties encountered in their preparation and use. Among these difficulties are the low range of colours attainable and inability to stand the weather. In fact, only the following pigments have been found suitable for use in silicate paints:—

For Blue.—Ultramarine and smalt.
,, *Yellow.*—Barium chromate, uranium oxide, and ochre.
,, *Black.*—Lampblack, boneblack, and graphite.
,, *Green.*—Chromic oxide, ultramarine green, and cobalt green.
,, *Red.*—Iron reds.
,, *Orange.*—Chrome red.
,, *Brown.*—Colcothar, burnt sienna, brown manganese oxide; these do not curdle the silicate.

For white, zinc white, white lead, and barium sulphate can be used only in small quantities and must be mixed with the silicate just before application.

The reds, chrome red and red lead, affect the silicate less rapidly, but still too quickly to permit of their use to more than a limited extent.

On the other hand, an admixture of casein with silicate paint retards the hardening of certain pigments, especially white lead. The mixture is easily prepared by triturating fresh curd with a little sodium silicate (density, 33° B.) to form a uniform mass and then stirring in the remainder of the silicate.

Milk Paints.—Pigments are mixed with milk and water to workable consistency, and then applied to a surface previously coated with silicate paint. When the milk paint is dry, it is topped with silicate paint by spraying.

1. *White.*

Milk	3 parts.
Water	7 ,,
Zinc white	10 ,,

2. *Grey.*

Milk	3 parts.
Water	7 ,,
Zinc white	10 ,,
Lampblack	½ ,,

3. *Light Green.*

Milk	2 parts.
Water	5 ,,
Zinc white	10 ,,
Green earth	5 ,,

4. *Yellow.*

Milk	2 parts.
Water	5 ,,
Ochre	10 ,,

5. *Brown.*

Milk	2 parts.
Water	5 ,,
Umber	10 ,,

6. *Red-Brown.*

Milk	2 parts.
Water	5 ,,
Burnt sienna	10 ,,

7. *Blue.*

Milk	2 parts.
Water	5 ,,
Ultramarine	10 ,,

8. *Black.*

Milk	2 parts.
Water	5 ,,
Ivory black	10 ,,

or—

Milk	2 parts.
Water	5 ,,
Colcothar	12 ,,

9. *Red.*

Milk	2 parts.
Water	5 ,,
Vermilion	25 ,,

No particular difficulty attaches to the compounding of pigments for casein-silicate paint, but care should be exercised not to employ pigments that harden rapidly.

CASEIN-SILICATE PAINT RECIPES.

1. *Blue.*

Casein-silicate vehicle	5 parts.
Ultramarine	3 ,,

2. *Yellow.*

Casein-silicate	5 parts.
Ochre	5 ,,

3. *Black.*

Casein-silicate	8 parts.
Bone or ivory black	3 ,,

4. *Green.*

Casein-silicate	5 parts.
Chrome green	11 ,,

5. *Red.*

Casein-silicate	5 parts.
Colcothar	4 ,,

6. *Brown.*

Casein-silicate	5 parts.
Brown manganese oxide	4 ,,

7. *White.*

Casein-silicate	5 parts.
Zinc white	5 ,,

8. *Grey.*

Casein-silicate	5 parts.
Zinc white	5 ,,
Lampblack	¼ ,,

or—

Casein-silicate	6 parts.
Zinc white	5 ,,
Lampblack	¼ ,,
Ultramarine	½ ,,

Trojel's Boiled Oil Substitute.—H. Trojel proposes to make a cheap substitute for boiled oil by carefully mixing together 100 parts of casein, 10 to 25 parts of soap solution, and 20 to 50 parts of slaked lime, 25 to 40 parts of turps being afterwards stirred in gradually, and the whole thinned with water to the consistency of boiled oil. If this preparation is to be kept for some time, a little ammonia is added, to prevent the casein settling out. The mass dries very quickly and can be mixed with colour for coating damp brick or wooden walls. It also adheres well to metal, and becomes insoluble in water on drying.

Calsomine Wash.—This preparation consists of a mineral base in combination with a binding medium having the property of solubility in water but reverting to a perfectly insoluble product when exposed to the air in the form of a coat of paint. This paint is therefore waterproof, possessing the properties of oil paint in this respect and being also capable of withstanding the influence of the weather. The pigment is a white or coloured powder consisting fundamentally of magnesium silicate or talc, which is added to the binding medium in the proportion of 90 parts to 10. It is also practicable to use 20 parts of lime, 70 of chalk and 10 of binding medium; these proportions again may be modified in turn. The binding medium is compounded of casein and lime, the former being obtained, as a dry white powder, by treating milk with an acid at 100° F. Sixty parts of this powder are mixed with 20 parts of dry slaked lime, whereupon the casein becomes soluble in water, though this property disappears on exposure to the atmosphere. Any convenient body colour may be incorporated with the mixture, and when the whole is thinned with water it furnishes an easy working and waterproof paint.

Quick-Drying Casein Paint.—When mixed with such volatile substances as turps, petroleum, benzol, etc., dissolved casein acquires the property of drying very quickly. Hence, by preparing a solution of casein together with oil or balsam, and thinning it with petroleum, a product is obtained which is quick drying as well as highly elastic.

A mixture of 8 parts of this medium, with about 10 of zinc white, lithopone, etc., forms a very useful light paint for outdoor or indoor use on woodwork or metal. It is worth noting that the addition of petroleum, benzol, or the like, causes the particles of the paint to penetrate deeply into wood and the fine joints in ironwork without stopping the circulation of air. This protects the iron from rusting;

while the antiseptic effect of the petroleum preserves wood from rotting and fungoid growths. Oil paint is soon spoiled in appearance when exposed to ammoniacal exhalations, but they have no effect on petroleum-casein paints. The latter dry readily and do not darken in course of time; neither does the smell of petroleum cling to them very long.

Petroleum may be replaced in these paints by benzol, turps, naphtha, xylol, and ethereal oils such as oil of spike lavender, etc. When the paint is to be used for outside work on timber or brickwork an addition of linseed oil is desirable, while the paint should be thinned down considerably so as to allow the particles to penetrate deep into the underlying material.

In places exposed to mechanical or atmospheric influences, or on damp walls, these quick-drying casein paints will be found highly advantageous.

Boiled Oil Substitute.—A substitute for boiled oil may be prepared by adding to 100 parts by weight of casein 10 to 20 parts of a 1 to 10 per cent. solution of soap, followed by 20 to 25 parts of slaked lime, the mixture being carefully kneaded until a homogeneous mass is formed. It is afterwards thinned by the gradual addition of 20 to 40 parts of turps and sufficient water to reduce the consistency to that of boiled oil. If the varnish is to be kept for any length of time, a little ammonia should be added to prevent the precipitation of the casein-lime complex. This substitute is much cheaper than boiled oil, and dries so quickly that two coatings of the paint made with it can be applied in immediate succession.

Casein Paint (German patent 186,272: A. Brunstein, Hamburg).—Casein, or other albuminate, is mixed to a stiff pulp with quicklime, chalk, and water, a slight current of air being then blown through the mass until it becomes fluid and gives off a faint odour of ammonia. Chlorinated, brominated or iodated oil is next stirred in, and the mixture is either converted into powder by trituration with chalk, or else diluted with water to a workable consistency. The oil is chlorinated by treating it with chlorine water and agitating the mixture until the oil has taken up a large proportion of chlorine. When bromine or iodine is employed, an alcoholic solution is used, the solvent being afterwards expelled.

Water-White Casein Varnish (German patent 200,919: M. Fehringer, Fuerth).—When an alcoholic solution of resin is mixed with an ammoniacal solution of casein, the resulting varnish, though drying with a high glass, is always cloudy, the material in suspension being incapable of removal by settling or by the use of clarifying agents. The inventor, however, claims that by exposing such varnish to a temperature below the freezing-point of water for some little time, it will separate into a clear, water-white layer and a cloudy stratum, the former being then removed by decantation.

Casein Paint.—Commercial casein 5 parts, barium sulphate 150 to 200, slaked lime 10, gum-tragacanth 5, glycerine soap in powder 3. A similar recipe to this in which formaldehyde is used is as follows: Casein 5 parts, ammonia 0·25, water 50, formaldehyde 0·5, barium sulphate 50 or upwards, linseed oil 5. The casein is mixed into a smooth paste with a little water, and thinned with more water. The lime or ammonia is added and causes the liquid to become thicker. Finally the pigment is incorporated, and the formaldehyde, if this is used.

Ring's Cold-water Paint.—G. R. Ring, of New Brighton, mixes casein or some other albuminous substance with a filling of levigated chalk, gypsum, lime, talc, pigments, etc., the whole being ground together. Glue or similar material is then mixed with hydraulic lime, and ground. The two fundamental ingredients thus obtained are mixed together, with a further quantity of filling material, to form the paint, which is thinned with water for use.

Formolactin.—Under this name the Aktiengesellschaft für chemische Industrie "Union," of Vienna, has put on the market a liquid intended for use as a wash or for printing on paper or analogous material in order to make the same washable, waterproof, and dustless. Formolactin is a concentrated solution of casein and formaldehyde, thick and milky in appearance.

When applied as a coating on any surface, formolactin also acts as a disinfectant. This disinfecting action can be renewed at any time by washing the surface over or spraying with a 1 per cent. solution of formaldehyde, without the use of any special apparatus, and without injuring the paper or any object in the room in the slightest degree.

On this account formolactin is highly suitable for painting bedrooms, hospital wards, smoking-rooms, living-rooms, etc., the cleaning of which is greatly facilitated by its use.

In consequence of its content of formaldehyde, formolactin destroys any nest of insects present in crevices in the walls to which it is applied.

The instructions for using this preparation are as follows:—

Formolactin is diluted with a 2 per cent. solution of formaldehyde, prepared by dissolving 5 parts of commercial 40 per cent. formaldehyde (formalin) in 95 parts of water. The degree of dilution depends on the amount of gloss desired and on the absorbent character of the wall-paper. Speaking generally, equal parts of formolactin and the said 2 per cent. solution of formaldehyde will be suitable for good ordinary wall-paper. If a higher gloss is desired or the paper is more absorbent, then 1 part of the 2 per cent. solution can be taken to 2 parts of formolactin. For a dull gloss and less absorbent paper the dilution may be increased to 1 : 2.

A wide, soft brush is used, and no more of the paint is laid on than the paper will take up, otherwise it will trickle down and a patchy appearance will be presented.

The colour of most wall papers is made to look brighter by a coating of this preparation, a fact which should be borne in mind when the paper is being selected.

After applying the coating it is left three to four hours to dry, and the room is afterwards well ventilated in order to remove the smell of the formaldehyde. This may be accelerated by sprinkling ammonia on strips of wadding and allowing it to evaporate inside the room. The smell of formaldehyde, however, is by no means injurious to health.

If the first coating does not produce the desired lustre, or fails to cover the paper properly, a second coating, properly thinned, may be laid on without affecting the durability of the covering.

The best way to wash and clean wall papers coated with this preparation is with lukewarm soap and water, to which $\frac{1}{4}$ to $\frac{1}{2}$ per cent. of commercial formaldehyde has been added as an antiseptic.

Waterproof Paint for Playing Cards.—Playing cards may be coated with a mixture of satin white—precipitated calcium sulphate—and an alkaline solution of casein. The coating is waterproof and washable, whilst still leaving the paper sufficiently absorbent to allow the cards to be printed in the usual way.

The best mixture for this purpose consists of 80 parts of satin white, 16 of casein, 2 to 4 of caustic soda or ammonia, and 25 or more of water. The inventor of the preparation believes that the satin white combines with the dissolved casein in such a manner as to render the latter insoluble when the coating has been applied and allowed to dry for some time.

This coating is said to be particularly useful in imparting to playing cards the desired enamel-like appearance, and to be capable of taking the most delicate multiple colour printing. The satin white may be partly replaced by blanc fixe.

Casein Colour Lakes.—The use of casein as a precipitant is useful in making colour lakes, kaolin being employed as the substratum. For instance, Dreher recommends grinding to a paste 30 parts of finely ground kaolin and 20 of lukewarm water, followed by a repetition of the operation with an addition of 80 parts of dissolved casein (10 parts of casein, 20 of water and 1 to 2 of ammonia). One hundred parts of dye solution (0·5 per cent. strength) are next added and well mixed, the whole being then treated with 2 parts of a 1 per cent. solution of tin tetra-chloride, added drop by drop. After being washed and pressed, the precipitate is dried at 60° C., or at 80° to 100° C. if the dye will bear that temperature. Both acid and basic aniline dyes can be precipitated on any substratum by this method. The resulting lakes are very bright in colour and are very fast to water. Tin tetrachloride may be replaced by other salts having an acid reaction, such as aluminium chloride, tin acetate, etc., but the acetate must be free from any excess of acetic acid, since this exerts a solvent action on the lake. The method is particularly useful for precipitating rhodamines and eosines, which it converts into extremely brilliant fine red lakes that are non-poisonous. The casein lakes also merit attention for coloured bookwork and litho printing, and for wall-paper and calico printing.

Paint for Marking Bags, Iron Barrels, Cases, etc.—A good paint which will adhere to fabrics, paper, wood, sheet-iron, etc., and is therefore suitable for marking and stencilling cases, wrappering, jute sacks, etc., is prepared in the following manner :—

About 20 parts by weight of water are heated to boiling in a glass vessel, and 1 part of aniline dye is stirred in, eosine being used for red, and phenol black or deep black for black. When this is dissolved, 2 parts of soluble casein are stirred in. If the liquid appears too thick when cold, and therefore difficult to lay on with the brush, it must be diluted with a corresponding amount of hot water.

The aniline dyes may be replaced by logwood solution and potassium chromate; but tincture of gall-nuts is not suitable for this purpose.

Stencilling paste is made by mixing pipeclay with ivory black or lampblack. The pipeclay (kaolin) is suitably coloured with aniline dye, carefully incorporated with the ivory black or lampblack, and then introduced into a thin solution of casein. After being put through a paint mill, the mass is packed in tin boxes.

Casein-Cement Paint.—Häusler recommended English Roman cement for this purpose. The boards to be coated are left unplaned, and pillars and beams are gone over with the roughing plane; the following method is recommended, and the wood will not only look like stone, but behave as though actually petrified:—

Two parts of English Roman cement is stirred up with 4 parts of washed scouring sand, 2 parts of fresh curd, and 1½ parts of skim milk, no more being made ready at a time than can be used up in an hour. While the mass is being applied, it must be kept continually stirred by an assistant in order to prevent the sand from settling to the bottom. The coating is laid on as thin and smoothly as possible, and as soon as it is dry is followed by a second. In summer it dries quickly and sets as hard as stone. Finally, woodwork that is to stand upright is coated with a mixture of boiled oil and an earthy pigment, a double coating being applied to sloping woodwork, and three or four coats on horizontal or exposed work that is liable to be trodden on.

For smoothly planed woodwork, Häusler used the subjoined mixture with equal success: English Roman cement, 4 parts; fresh curd, 2 parts; buttermilk, 1½ parts; the whole being well stirred together and made up in sufficient quantity to last only for a short time. The Roman cement must be of good quality, preferably freshly burned.

CHAPTER VI.

THE TECHNICS OF CASEIN PAINTING.

Casein painting is based on the principle that casein possesses the property of forming extremely resistant and permanent compounds, both with the pigment and also with the substratum. The subject is, therefore, divisible into several sections, *viz.*:—

1. Preparation of the ground.
2. Preparation of the binding medium.
3. Preparation and application of the casein paint.

Although from its nature casein painting is no more difficult than any other branch of the art, certain precautionary regulations must nevertheless be observed in the preparation of the ground or surface to be painted on. In the first place, surfaces of solid and granular lime- or cement-plaster; surfaces already coated with a layer of oil paint, and surfaces consisting of ordinary building stone, or ornaments of clay, wood, sheet metal, etc., must be thoroughly cleaned before painting is begun. If casein paint is to be applied to rough lime plaster the latter must be brushed over with diluted milk which has been carefully skimmed and mixed with the right quantity of water. Defective places in the plaster of house fronts must be patched up with mortar, or preferably with a mass composed of 1 part of patent lime and 3½ to 4 parts of pure sand. Patent lime is made by allowing solutions of tin and zinc chloride to act on lime, and it will also bear additions of ground marble, cement, and earthy pigments.

New cement plaster, or such as exhibits fine cracks, moisture or efflorescent salts, is best washed over with dilute hydrochloric or sulphuric acid (1 part of acid to 8 to 10 of water), and after a short time has elapsed wiped with a rag and left to dry. A preliminary coating of caoutchouc butter, Kesserl's fluoride paint or diluted blood, etc., is also advisable.

For indoor use the ground should be impregnated with alum, 1 part of which is dissolved in 5 of hot water and then diluted with 10 parts more of the latter. This soaking, however, is only needed for walls that have previously been coated with lime paint or distemper. Gerhardt's paint soap is also recommended for the same purpose, its antiseptic properties and power of rendering animal matter insoluble fitting it for use on articles where fungoid growth is possible. The penetration of this preparation into the ground increases the durability of the casein paint, especially if the alum impregnation and Gerhardt's soap treatment be combined.

Joints, cracks, or holes in brick or woodwork must be filled up with undiluted casein paint; but large fissures are best stopped with casein putty.

If there are any damp places in the plaster, and it is desired to prevent them showing through, they should be impregnated with a thin solution of shellac before the paint is applied. Certain impregnating varnishes are also sold for this purpose.

Metals, such as zinc, copper, and iron, may be painted with quick-drying casein paints without any preparation, provided the surface is clean and not covered with a film of oxide. Should this, however, be present in the form, say of iron rust, it must be removed, by washing with caustic soda and petroleum or by scratch-brushing.

Finally, in the case of objects that are to be decorated, it is necessary to provide a non-absorbent surface, to form a suitable ground for painting on. A special preparation is required for fresco painting, it being essential for the ground to be thick and dry, so as to prevent the appearance of any efflorescence from the brickwork underneath. For this reason, the plaster should be composed of as many layers as possible, each dried separately. Two to four strata of coarse plaster and an upper one of fine plaster are usually sufficient. Each layer should be thoroughly dry before the next one is put on, the surface being well moistened with water just before the succeeding coating is applied. The bottom layer must be coarse grained and thicker than the others, the total thickness being 1 to 2 inches.

The coarse plaster is prepared of mortar from 1 part by volume of patent lime and 2 parts of clean, coarse, sharp sand (preferably quartz sand), burnt fireclay or powdered stone, together with about 10 per cent. of good Portland cement. This mortar is applied to the wall surface, beaten with a wooden bar to drive out air bubbles, and left to dry for as long as possible. On this surface, after wetting it with pure or boiled water that has been allowed to cool, the fine plaster is applied, the mortar for which is compounded of 1 part patent lime, 1 part fine, sifted, dust-free, clean sand and 1 part marble sand, the whole mixed with water that has previously been boiled. This mortar is also beaten to expel air bubbles in the mixing trough, and is then laid on over the coarse plaster. As soon as the surface has dried dull, it is wetted with a little boiled and cooled water and worked over with a smoothing board, any residual roughness being smoothed away by a sheet of zinc after the mortar has set to such an extent that it merely yields a little under the pressure of the finger. Directly this upper layer is dry it can be painted on with the necessary casein paints, and retouched with the same colours after drying.

To facilitate the fresco painting the upper layer of plaster can be put on in sections, or else kept soft for a considerable time by wetting it with water that has been boiled, or by hanging wet cloths over the surface. This prevents the too rapid crystallisation of the lime, which would otherwise occur.

Dry fresco painting is performed in the following manner: Old or dry plaster walls are scrubbed with a stone until the upper surface has been worn away and the sound absorbent plaster is reached; but if the crust is sound and rough grained it need not be removed. A mixture of fluid casein medium, white outdoor cement and 10 per cent. of calcined magnesia is then mixed and diluted with previously boiled and cooled water, the first coating being thinner than the others; and, the wall having been damped with re-cooled or rain water, several coatings of this mixture are applied in succession. As soon as the surface has dried dull, several coatings of ground colour are laid on, and the decorations and painting are then applied.

According to Martin, the aforesaid outdoor cement is also known as "white Portland cement," and is prepared by mixing 1 part of iron-free kaolin, 3 to 5 parts of pure white chalk, followed by 2 to 5 parts of gypsum or 3 to 5 parts of magnesium chloride. The ingredients, wet or dry mixed, are calcined in an oven.

Probably the best method of imitating the old Pompeian wall paintings in character and durability is the dry fresco process of Gerhardt. In some cases, however, it is possible to dispense with scouring the walls beforehand, replacing this treatment by the less troublesome process of soaking the walls several times over with paint soap at the completion of the work, this treatment increasing the brightness of the colours and improving their character and durability.

After the impregnated surface has dried it may be polished to a dull gloss with a brush. The precautions specified must, however, be adopted in order to secure the intimate connection between the painting and the ground, so necessary to render the painting durable.

Compounding the Binding Medium.—Next to the substratum, the most important thing in casein painting is the medium, since on this depends not only the durability of the paint but also several of its chief characteristics. Hence, it can be easily understood that the composition of the medium may vary in many ways, according to the purpose for which it is intended. Thus, one used for ordinary painting on walls is not also suitable for decorative painting, whilst, on the other hand, a medium for indoor work cannot be employed for outdoor painting.

Casein and its properties have been already described, therefore all that is now necessary to mention is that the dry casein must be converted into a soluble form before it can be used as a binder.

The usual solvents for this purpose are caustic potash or soda, borax, sodium bicarbonate, ammonia, potassium or sodium silicate (water-glass), slaked lime, cement, etc. Since it would not pay the painter to prepare casein from milk, it is preferable to use the commercial soluble casein. A simple solution of this is made by adding to 1 part of casein 0·3 to 0·4 part of strong ammonia, the solution being protected from putrefaction by means of a little carbolic acid. To convert these solutions into a usable medium they are treated with a little alkaline solution of rosin, containing a small admixture of soap or wax. These latter substances are intended to surround the particles of pigment with a protective envelope against atmospheric influences. A medium prepared in this way is suitable for fine artistic painting indoors, enabling different pigments to be used and imparting to these a fine sheen.

Another casein medium, for which, however, the same claims cannot be advanced, is prepared by intimately mixing an alkaline solution of casein with diatomaceous earth (*kieselguhr*). This has the drawback of becoming dark-coloured in time, and not being suitable for use with certain pigments, such as Berlin blue, though it can be usefully employed for coloured paints and rough ornamentation work.

On the other hand, compounds of fatty acids with alumina, and similar substances, are not advisable. Prof. Linke, in his work on painters' colours, says of these that though, when first dried, they form a dense, horny layer which repels water, the colours prepared with their aid soon alter in molecular structure on exposure to the air, and fall to powder, which is readily oxidised by atmospheric oxygen, becoming chemically changed and therefore rendered useless.

If dissolved casein is emulsified by oil, balsams, or fats, together or separately, the resulting medium is distinguished by the property of leaving the natural tone of pigments unaltered. A casein medium of this kind, or one treated with rosin, cannot, of course, be thinned with water, but only with benzol, petroleum, turps or other volatile substances.

All the media hitherto described are more or less restricted to use for indoor painting. For outdoor use the casein must be incorporated with substances with which it forms insoluble compounds. The best known of these is slaked lime, which has been already mentioned in connection with cold-water paints (*q.v.*). Cement also forms with casein a particularly resistant and effective binding medium, a patent for making these media having been granted to Ant. Richard of Düsseldorf. According to this specification, casein, properly freed from fat, is mixed with an antiseptic, *e.g.*, formaldehyde, carbolic acid or the like, and then carefully ground along with water. The resulting thin liquid mass then receives an addition of cement proportionate to the amount of casein present, the whole being well mixed and left to stand until the thicker, heavier constituents have settled down, whereupon the supernatant liquid, which forms the medium, is separated by decantation. This liquid has not the slightest action on the most sensitive body colours, and its binding power is unaffected by formaldehyde. It renders the colours thoroughly workable and imparts great durability, so that they can also be used for outdoor work, being able to withstand the weather. These colours are also suitable for use in calico printing, since they are insoluble in water when once dry. The sedimental matter can be ground and used as a cover paint.

The Preparation and Application of Casein Paints.—To prepare artists' colours with casein, all that is necessary is to take one of the media just described and mix it with the appropriate pigments. The pigments most suitable for *white* are: barytes, China clay, Paris white, lithopone, and zinc white; for *yellow:* cadmium yellow, golden or pale ochre, Naples yellow, "satinober," Schütt yellow, and Terra di Siena; for *red:* colcothar, carmine, chrome red, fast red, Indian red, madder lake, red lead, signal red, Terra pozzuoli, vermilion, and vermilionette; for *brown:* asphaltum, Cassel brown, dark ochre, manganese brown, Terra di Siena, umber, Vandyke brown; for *blue:* indigo, cobalt blue, blue-green oxide, and ultramarine; for *green:* chromic oxide green, green earth, cobalt green, permanent green, Schweinfurt green, and emerald green; for *black:* ivory black, bone black, lampblack, and Paris black.

To prepare small quantities, the binding medium is mixed with the dry pigments on a plate or sheet of glass, or else they are ground with a muller or in a paint mill. The resulting paint is thinned to a workable condition with boiled and re-cooled water at the time of application.

For making up large quantities at a time, the dry colours may be saturated with water and then mixed with the casein preparation. In the case of heavy pigments, this precaution is advisable, since the mixture is easily rendered too thin. The colours, however, adhere better when mixed with the binding medium dry, the particles, in that event, absorbing the vehicle instead of water, thus becoming more completely enveloped by it.

Some of the organic colouring matters, *e.g.*, bone black, Cassel brown, etc., which form a good nutrient medium for mould fungi, require an addition of ½ to 1 per cent. of carbolic acid, 1 per mil. of formalin, or about 2 to 3 per cent. of salicylic acid solution, to the water to preserve them; this admixture causing no harm in the case of other colours.

Although not essential, it is advisable to add a little lime to casein paints, especially when they are in paste form or for outdoor use.

If the amount of lime to be added is large, it is better not to make up a large stock of the paint, but only just enough for two to three days' consumption, since the insolubility of the paint film becomes greater when the combination of lime and casein is fresh but is lessened when the mixture is stale.

The proportions of medium and pigment cannot be arbitrarily laid down, owing to the divergent requirements of the various pigments, and also because one and the same pigment varies in this respect, according to its origin and mode of preparation, apart from the fact that the power of the different casein media is a variable quantity.

Chalk and calcined earth pigments require a larger proportion of casein medium than lithopone, white lead, etc., whilst ochre and other raw earths usually need less. Light colours generally take less than dark ones, and inorganic pigments less than those of organic origin. Usually the quantity of medium varies inversely as the specific gravity of the pigment just as in grinding oil paints.

The proportion of medium also varies according to the surface to be coated. For example, a larger proportion may generally be used on solid plaster and other solid substrata, such as metal, cement, oil paint, paper, canvas, etc., than on a surface that readily chips, such as plaster of Paris. In any case, if the paint is too strong it is very liable to cause the weak substratum to break away, chip, or peel off, especially when organic colours are used.

For painting on solid or prepared plaster, rough wood, etc., sufficient casein medium must be taken for the paint to adhere strongly to parchment paper when dry, so that it does not peel off when the paper is folded, and will stand the action of a strong jet of water at the end of about twenty-four hours.

To ascertain whether the right proportion of medium has been used, a small quantity of the paint is brushed on a sheet of writing or printing paper. If the paper is found to have shrunk much when the paint is dry, too much medium has been used.

As regards the handling of the brush, this is similar to distemper work, only that the brush must be more frequently cleansed with soap. A peculiar kind of curdling can be noticed when the paint in the can or brush has become too dry, and an attempt is made to reduce it with water. In such a case the brush must be washed with soap and water and a fresh quantity of paint taken. Hence both paint and brush should be kept moist, and the colours on the palette frequently sprayed with water, the can being kept covered up, and preferably fitted with an airtight lid.

In connection with the storing of casein paints the following points may be mentioned: In order to prevent the medium from drying, the can is either turned upside down, or else the surface of the paint covered with a layer of water. The paint, however, must not be thinned with this water, or a separation into layers may easily occur.

If the paint and medium separate in the can, they may be remixed by stirring or shaking, but any skin that forms should be thrown away.

Casein paint that has partly or completely dried in the can is unfit for use, and it is therefore necessary to guard against this by covering the surface with water or closing the cans airtight.

If the medium becomes frozen in winter it should be slowly rewarmed over a water bath and then stirred up well.

The application of casein paints is performed in the following manner :—

After the ground has been suitably prepared, the outlines are sketched with crayon and coloured in, any excess of crayon being wiped off with a soft clean cloth.

The well-thinned paint is then laid on, as light in colour as possible. The oftener the coating is repeated, the more attractive the effect produced, whereas, if the paint is too thick the effect is diminished and it readily tends to peel off, this being especially the case with dark colours containing an excess of the casein medium, though it may also occur when the other extreme is in question. This must be tried and modifications made accordingly before beginning the actual work of painting.

Both wide bristle brushes and fine long sable brushes are used. If, when the work is finished, some of the tones do not harmonise, they can be modified by working over the whole portion.

Thus, if one tone be too light and warm or too bright, it is worked over with ivory black alone, other alterations being made with deep colours, reduced to a thin paste with water and quickly laid on with the brush. In these operations the greatest cleanliness is necessary, both with the colours and with the cans and other utensils.

To paint frescoes on canvas, a rough canvas is coated with undiluted casein preparation and painted in quite wet with colour that has merely been mixed with water without any casein medium. At the same time the under layer is kept well moistened with water throughout the entire process. If the dried paint is to be topped, the surface must be sprayed with the casein medium diluted 8- to 10-fold with water, and the paint applied as above.

In painting pictures on outside work, the casein medium prepared with the assistance of oil, balsams, and fats, or wax and resin is used. For the first coating on absorbent surfaces this is mixed with ordinary amber varnish which improves the drying properties and furnishes a handsome gloss.

If, on the other hand, drying is to be retarded in order to be able to work the colours together longer, then a little oil is added to the medium or the same is mixed with oil paint. Should the surface nevertheless get too dry, the true shade of the colours may be revealed by moistening with turps.

To coat the pictures with glossy varnish, as though they were oil paintings, a coating of glossy varnish or some other thick varnish must be brushed in, and when this is dry it should be covered by a second coat of varnish.

The varnish may be replaced by a coating of wax solution, the dried layer being heated to melting-point in order to increase the durability and powers of resistance. The same purpose is also served by the paint soap and impregnating varnish, as well as the formaldehyde solutions already mentioned, though these can be used only on casein paintings that are free from fatty matters.

A fixative of this kind can be prepared by treating an aqueous solution of casein and borax with absolute methyl alcohol free from acetone, the solution being left to stand for a long time and separated from the sediment.

According to Chialiva and Dupot, in their patent specification, this fixative has the property of drying quickly and not too glossy.

Another weatherproof varnish for preserving paintings is obtained, according to the patent of Gebrüder Pilz, by moistening collodion cotton with methyl alcohol and then dissolving it in a solution of camphor in alcohol containing spirit of turpentine.

Formaldehyde, too, has latterly been recommended as an excellent means of rendering casein paintings insoluble in water (see Formolactin). If a dry picture, painted with casein paint, be exposed to the vapours of formaldehyde, the agglutinant in the paint (casein, glue, or albumen) quickly becomes waterproof.

Before closing the present chapter, it should be stated that painting in the fresco and encaustic styles, as also *al secco* and *al sgraffito*, can be performed with casein paints. The methods elaborated by the Düsseldorf artist, Fritz Gerhardt, on the basis of prolonged investigation and chemical progress, are founded on a special preparation of the substratum and on the use of specially prepared colours. These include the fresco colours, marble colours (containing marble dust and casein), encaustic colours (prepared with wax and resin), the spike-oil colours and the universal colours. The Gobelin colours (imitation Gobelins) and flag colours, used for decorating flags, also belong to this class.

Finally, tempera painting can also be performed with casein paints. According to Beissier, a colour of this kind can be prepared by mixing—

Dry casein powder	7 parts.
Slaked lime	20 ,,
Covering mass (chalk, ochre)	100 ,,
Dextrin	8 ,,
Soap powder	8 ,,

and the necessary body colour.

The wall pictures in the Hall of Fame (Ruhmeshalle) in Berlin were painted in lime tempera by Professor Geselschap. The medium, consisting of three parts by volume of fresh casein and one part of lime, was prepared fresh every day and ground along with the colours.

It is now generally admitted that paintings executed in casein colours will remain unaltered in tone for years and effectually resist atmospheric influences. They also exhibit extraordinary brightness, a fine velvety sheen, and clearness in the shadows. In contrast to other processes, it is possible with casein colours to paint the same surface over and over again, the effect gaining in beauty and solidity with each application. Finally, the paintings can be executed on any solid ground, and are easily cleaned when they become dirty. On account of these advantages casein painting is gaining ground, and a number of casein preparations for this purpose are on the market, though they cannot be discussed within the limits of the present work. In this connection a thoroughly scientific investigation of casein painting—on the same lines as that which has already been made in respect of oil and mineral paints—is highly desirable.

The Value of Casein Paint.[1]—Though it has long been known that casein combines with certain substances to form agglutinant compounds, which become more or less insoluble on exposure to air, and though it has been known that casein has been detected in old paintings, many of a decorative nature, yet it is only within the last fifty years or so that any extensive use has been made of it for this purpose.

That an addition of milk to limewashes greatly increases their durability has long been known, and in fact such a mixture constitutes the first casein paint, the casein of the milk forming with the caustic a compound which is the basis

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[1] From a paper read by H. Clucas, Toronto, at the 1914 Convention of the Master House Painters and Decorators of Eastern Canada.

of all such paints. The casein is rendered soluble, a result that can be produced, not merely with quicklime, but also with various substances having an alkaline action.

These are met with in commerce in the form of paste or liquid, containing the casein in a dissociated condition, and in some cases, already mixed with other substances used in paint, such as linseed oil, boiled oil, varnish, resin, or petroleum, in order to produce special effects. Others, and these the most important of all, are supplied in the form of powder by the makers, and contain casein and alkali in the dry state.

It is only when these paints are mixed with water to make them fluid for use that the alkali is dissolved, and in turn acts as a solvent on the casein.

Making this powder up into paint is a comparatively easy matter, though a certain amount of care is necessary to insure good results. The operation may be performed in any vessel that is clean, and free from grease, in the following manner:—

Fifty parts of water are added by degrees to 100 parts of the powder, with constant stirring, which is continued until the mass is homogeneous and free from lumps. The mass is then covered with a thin layer of water and left for about half an hour, after which it is again stirred, and more water added until a workable paint is obtained, about the consistency of oil paint. The paint should be used without delay, hence it is desirable not to make up any more of the paint than can be used the same day. A solid and clean surface is essential to success, as the paint will adhere to any solid surface, such as lime, plaster of Paris, cement plaster, brick, stone, or wood, as well as canvas without any preparation, all that is necessary is to clean the surface of dust or dirt and begin painting at once. The paint dries very quickly and as smooth as enamel, and in forty-eight hours can be washed. On account of its elasticity it can be used as a primer under paint, varnish, or enamel. If applied on a firm substratum it will neither crack nor peel off; but the surface must be free from old coatings of lime or kalsomine washes. It has been found both in the United States and Canada that the main reason why casein paints did not become popular as quickly as they deserved, was the fact that any old kalsomine coat or lime wash had to be washed off to the very last degree, because if any of the old washes, even to the eighth of an inch, were left around the window frames or door posts, and was covered over with casein paint, the strong binders in the latter pulled off the weaker under coat and caused a ragged appearance. Even the smallest part would cause the paint to peel off even a little further than was warranted by the under coat which was left (painters will understand this action).

Further, all casein paints have the advantage of drying quickly, and being easy to work without requiring special preparation of the surface to be painted, except that already mentioned. It dries without gloss on brick, stone, plaster, wood, or canvas, without stopping up the pores of brickwork. These paints are soaked in cold water in order to swell up the soluble binding constituents, salts, and similar compounds, so that they may dissolve completely when diluted further with cold water, and also perform their chemical functions.

In addition to the binding constituents the paint powders of this kind contain mineral material, such as Paris white, zinc oxide, lithopone, forming the bulk of the mass of the given covering power, while the body colours are also present to produce the desired shade of colour.

These pigments which are present in merely minute proportions, in case of light colours, must be perfectly indifferent to lime and alkali; a green, for instance, compounded with

Prussian blue and chrome yellow cannot be used. The pigments must be as pure as possible.

After a coat of casein paint has been applied, a second chemical action takes place, by which, through exposure to the air, the quicklime which has caused the casein to become soluble, is changed into carbonate of lime and both the casein and lime are then insoluble, the casein having come back to its original form, as pure casein is not soluble in water, hence the necessity of the lime to work it.

Notwithstanding their power of standing the weather, cold water casein paints are porous, and do not prevent the circulation of air. On account of their good qualities these paints are in frequent use, both for outdoor and indoor work.

To the practical man there may be a doubt that cold water casein paint is a cheap way of doing things, as compared with white lead and oil, but expensive methods do not always yield the best results. Casein paints have been and still are much in evidence in European and American summer resorts, and more especially on such work as factories, hospitals, dormitories, garages, fences, boat houses, and many summer cottages show evidence of its decorative and sanitary purposes.

Cold water paints with casein binder and containing antiseptics, have proved to be of greater durability than the bulk of the ordinary water paints, on account of their resistance to atmospheric influence and dampness, where the cost of oil paint is prohibitive.

In concluding, I would mention one more of the many purposes that casein water paints can be applied to and prove itself invaluable to the present need of the trade, *viz.*, on concrete and cement work. On a floor, a coating of fresh cement was applied about three-eighths of an inch thick and as soon as this was thoroughly dry (after three days) a coat of white casein paint was applied. This coating was allowed two days for the necessary chemical change to take place, as described previously, and then a coat of ordinary floor paint was applied and allowed to dry in the usual way. This floor paint was found on careful inspection to be just as sound as if it had been applied on a wood floor, or over a primer, and did not crack or give way when loaded trucks were wheeled over it.

CHAPTER VII.

CASEIN ADHESIVES AND PUTTIES.

THE employment of casein as an adhesive substance is not modern. It is only within the last few years that it has received any marked attention, and has been placed on the market under various names, such as casein glue, cold glue, cold-water glue, caseogum, gluten, etc., these being not merely suitable for industrial purposes, but also, mainly, for replacing glue in the wood-working industries. Though many of these preparations comply with all the requirements of a glue substitute, and possess the additional advantages of being inodorous and ready for immediate use without previous soaking and heating, they have not become popular to any very great extent. There is, however, very little doubt that the prejudice against them will not continue when their advantages are made fully known.

The raw material for these casein adhesives and putties is the fat-free casein obtained from curdled milk reduced to a liquid or pasty form by the aid of such chemical agents as the alkaline earths, their salts, ammonia, tungstic salts and water. The products thus formed are ready for use; but analogous products in the form of powder can be prepared from casein that has been dried out of contact with air, then ground and mixed with the solvent reagents in their dry state. In general, casein glue ready for use, *i.e.*, mixed with water, has been more successful than the dry powder, but the latter is probably more convenient when intended for distant destinations.

The casein is prepared from milk in the usual manner, by the addition of acids—acetic acid, tartaric acid, etc.—the casein being accompanied by a certain unavoidable small proportion of fat. Although weak acetic acid is usually employed for precipitating casein from skim milk, it is not the only acid used, as occasionally sulphuric or hydrochloric acid may be used in place of it, this accounting to some extent for the variations which are found in commercial brands of the material. After precipitation the casein must be neutralised before it can be treated further, for which purpose it is steeped in a solution of lime (lime-water) until it no longer reddens blue litmus paper. This treatment furnishes soluble calcium acetate, which must be washed out before the casein can be converted into glue. For this reason Bellamy recommends that the casein should be precipitated by means of vegetable substances, whose coagulant properties are based on the presence of tannin, *e.g.*, cutch, China bark, oak bark and other barks, sumach, etc. Special success has attended the use of wild-cherry bark (*Prunus virginiana*) for this purpose. The resulting casein does not require neutralising, and is easily worked up, besides being more uniform in quality. At the same time, the quantity of the precipitant is immaterial, since any excess remains in solution and therefore does not remain with the casein when this is boiled. Whatever method of preparation is adopted, it is always advisable to add to the casein a little sodium arsenate, Na_2HAsO_4, or some other salt of arsenic, since this increases its adhesive power and forms a kind of chemical mordant.

Another method of preparing casein specially for use as an adhesive is the following: Milk is left to stand in a cool place and the cream carefully skimmed off, this being repeated as long as any cream continues to rise, the milk being heated after souring to make it curdle. To test whether all the casein has been precipitated by the lactic acid of the milk, a sample of the separated liquid is treated with a little hydrochloric acid; if a precipitate is formed there is still some casein in solution, and this should be separated by the addition of 1 per cent. of hydrochloric acid, without waiting any longer for it to curdle. The curd is next pressed and washed with soft water until the washings are free from all trace of acid. To remove the final particles of fat the curd is boiled up with water and spread on a filter cloth.

When dry the curd is pressed and dried, first at a moderate temperature, then with an increased application of heat, and finally in a partial vacuum, if necessary. In this way it can be obtained either in the form of fine granules or as a horny shrunken mass. In either case it will keep indefinitely, but is liable to insect ravages, and especially to those of certain larvæ.

Casein Glue.—According to the "Revue des Produits Chimiques," "casein glue is prepared by dissolving fat-free casein in a saturated solution of borax, the resulting concentrated solution having strong adhesive properties and finding extensive employment as a substitute for glue and gum-arabic". The borax solution is prepared by dissolving 1 part of borax in 12 parts of cold water, the casein being then added, little by little.

To prepare casein cement, curdled milk is triturated in a mill and with successive additions of slaked lime until a compact mass is formed. This must be used almost immediately, since it hardens very quickly.

Casein dissolved by a solution of carbonate of potash or soda also forms an excellent cement. The most suitable proportions for the mixture are 5 parts of powdered casein and 1 part of pulverised burnt lime, mixed together with sufficient hot water to make a thin paste. Casein for cement may also be prepared from skim milk, by drying the latter in thin layers, reducing the product to powder and mixing it with 1 part of quicklime and enough water to form a paste. Blood albumen may be used in place of casein for certain purposes, its insolubility in water after exposure to a temperature of 40° C. being utilised in the paper industry. A weatherproof paint may be prepared by replacing casein by finely divided glue, the colours being ground with size, gelatine, or gum-arabic, and applied to the surface to be coated. While the paint is still fresh it is treated with a 1 per cent. solution of bichromate of potash, which solidifies the coating and enables it to stand washing. The same result may also be obtained with a 20 per cent. solution of chrome alum, rendered slightly alkaline with ammonia.

Casein Glue in Plates or Flakes.—One hundred and fifty parts of purified dry casein are mixed with 75 parts of a solution of sodium tungstate and well stirred. The mass is then thickened at a moderate temperature in a jacketed enamelled pan (or on the water bath), *i.e.*, is concentrated as far as possible, and is then cast into moulds or poured out on a sheet of glass or a marble slab. If moulded it can be cut into flat slabs like glue and dried on trays; but in the other case, according to the percentage of water present, it forms a more or less solid mass, which readily dissolves in hot water.

Bolder's Liquid Casein Glue.—H. Bolder, of Charlottenburg, prepares a glue possessing the same adhesive properties as ordinary joiner's glue, but in a liquid form, which is ready for use without warming and is capable of resisting moisture, by treating dry casein with a dilute solution of borax, or with sufficient ammonia to produce a faintly alkaline reaction. This preparation may be used or mixed with liquid starch in any proportion.

Crosspietsch's Adhesive.—A mixture of casein, castor oil, and linseed oil, thickened by heat, is treated with alum, sugar-candy and dextrin, and heated until a homogeneous mass is formed, which is then treated with water-glass.

Jeromin's Casein Adhesive.—According to German patent 154,289, lime, sodium-silicate and casein are mixed together and applied to the wood to be glued, left to dry and afterwards heated, with application of pressure, to form a waterproof joint. This method of mixing the three ingredients direct has the disadvantage that the casein is not fully acted upon; and it is found that the adhesive is more powerful when the casein has been treated with lime water before mixing it with the sodium silicate and lime.

The method of treating casein with lime or alkalies is not new, as a process of this kind is described in German patent 116,355, though the purpose of the treatment in that instance is a different one, namely, the production of a viscous solution of casein. With this object the casein is treated with sufficient alkali to produce a faintly alkaline reaction, that is to say, the amount of alkali added is in slight excess of that necessary to neutralize the casein. This implies that the casein is in the form of a solution and is no longer in the gelatinous form, which solution, however, is incapable of fulfilling the purpose for which it is intended, namely, that of an adhesive and filler. To overcome this drawback the casein is reconverted into the colloidal state by means of tannin, so that the final product is improved both as to its adhesive and its filling power. Hence the method consists first in preparing a non-adhesive solution and then converting this into an adhesive by partial precipitation of the casein.

On the other hand, Jeromin proposes to effect the same result in a more direct manner. The dispersal and solution of the casein by alkalies is in this case avoided, lime water being used to make the casein swell up. In certain circumstances the whole of the lime can be added at once; but this is attended with the aforesaid drawback of unequal distribution of the casein, a contingency that is overcome in the present case by the preliminary swelling of the casein in a small quantity of lime water. It must be remarked, however, that in the subjoined recipe the quantity of lime water mentioned does not contain enough lime to produce the maximum effect, though it is sufficient to cause swelling and thus prepare for the formation of a homogeneous mass through the subsequent mixing and combination with the lime which is subsequently added.

The method is performed as follows:—

Twelve and a half pounds of ground casein powder are mixed with three times its weight of clear lime water, stirred up in the same and left to settle for about forty-eight hours. When the casein has absorbed the whole of the liquid, the mass, weighing about 50 lb., is mixed with 2½ lb. of lime and 25 lb. of water, the whole being kept well stirred for about twenty minutes, after which 17½ lb. of water-glass are stirred in. When this mass has stood for a while it may be further diluted if necessary.

In this manner a very uniform and effective adhesive is obtained, one far superior to that furnished by the process described in the German patent 60,156.

The whole of the casein is acted upon, no unaltered particles being left in the mass, as hitherto, such particles being a source of weakness to the adhesive when placed under heat and pressure, at the same time they diminish its waterproof properties and, moreover, absorb moisture which leads to putrefaction and decay.

The use of lime for this purpose was also patented by C. W. Luther (English patent 6104, 1892).

Hall's Casein Glue.—A powerful fireproof glue is obtained, according to W. A. Hall (English patent 2949, 1903), by mixing—

Dry casein	50 to 60	parts	by weight.
Sodium phosphate	20	,,	,,
Sodium sulphite	10	,,	,,
Dry lime, slaked or burned	20 to 30	,,	,,

In another of Hall's recipes an adhesive is prepared by modifying starch under the influence of heat, and stirring this product with casein until the whole is nearly or quite absorbed by the particles of casein, a solution of alkali being added during stirring. By the intimate admixture of the several ingredients a very useful adhesive is obtained.

Still another process consists in combining certain proportions of casein, ammonia, and formaldehyde to form a mass suitable for sizing paper, straw, etc.

In a patent granted to W. A. Hall, Assignor to the Casein Company of America (U.S. patent 758,064, April 26, 1904), a mixture is made by incorporating a solution of "modified" starch with casein and adding an alkali and other ingredients during the process.

Waterproof Glue.—A waterproof glue or putty is obtained by mixing an albuminous substance such as casein, albumen, etc., with a caustic alkali (potash, soda or lime) or a carbonate, silicate, borate or phosphate of soda or potash. The inventor states that when an excess of alkali is present the product soon becomes insoluble in water at the ordinary temperature. On the other hand, when the albuminous substance is in excess the conversion proceeds slowly, but is accelerated by heat. In using the latter preparation, the surfaces to be joined are coated with the mixture, left to dry, and then pressed together between hot rollers. Inert substances may be added to the mixture.

Liquid Casein Glue.—To prepare a stable casein glue, which will dry or set immediately and then resists moisture and the influence of weather, 10 parts by weight of fresh curd are mixed with 6 parts of water to a thick cream, warmed to 40° C. and more water added with a few drops of ammonia, the liquid being allowed to stand till the casein is fully precipitated. This furnishes pure casein, and the whey can be eliminated by draining, pressure, or centrifugalising. The resulting casein is washed by spreading it out on a stretched cloth and pouring water over it.

The product is next mixed with ¾ to 1 part by weight of strong ammonia solution in a pan and heated to 30° to 40° C., whereby it is converted into a liquid glue, which can be diluted with about 80 per cent. of water and preserved by an addition of carbolic acid or thymol.

To make a quick-setting joint with this preparation, it is laid on with a brush, and left to dry, the surfaces being afterwards brushed over with milk (or thin cream) of lime and pressed together. The calcium of the milk of lime combines in the joint with the casein of the glue, ammonia being liberated, the resulting calcium complex fixing the surfaces so tightly that the joined article can be worked five minutes afterwards.

The ammonia can, of course, be replaced by caustic potash, caustic soda, or any other alkali, but the presence of such alkalies renders the glue more sensitive to moisture.

Powdered Casein Glue.—Dried, purified casein, 15 to 20 parts by weight, is ground to fine meal in a pulveriser, and then incorporated, in a sifting and mixing machine, with 1 to 4 parts of ground borax or 2 to 8 parts of sodium bicarbonate, great care being bestowed on proper mixing.

Casein and Borax Glue.—This is a solution of casein in a saturated solution of borax. It has a transparent, gelatinous appearance, and when dried forms a yellowish-white, somewhat brittle mass, which is readily soluble in water, has high adhesive properties and is suitable for cabinetmakers' use. It is prepared by setting milk to curdle in a warm place, the completeness of the operation being tested with hydrochloric acid, 1 per cent. of which is added to the milk if the test indicates that casein still remains in solution. The purification and drying of the casein are performed in the manner already described at the commencement of the present chapter. For use, the necessary quantity is placed in a suitable vessel and mixed with levigated chalk, slaked lime, water-glass, and borax solution, an excellent adhesive being thus obtained.

According to another report, this product is prepared as follows: Milk is heated with a little tartaric acid, or when large quantities are to be produced, is curdled in the ordinary way as for cheese-making. The resulting curd, in a still moist condition, is sprinkled with a solution of 6 parts of borax in 100 parts of water, and gently warmed and stirred, the casein being thereby dissolved. The clear solution is a strong adhesive, cheap and durable, and can be used to replace gum-arabic in all cases where dextrin would be unsuitable.

Casein for Mending Glass, China, etc.—Take one quart of milk and stir into it 120 grains tartaric acid, gently heating until it coagulates.

Drain off the casein and dissolve it in a 6 per cent. warmed borax solution, *i.e.*, just sufficient to liquefy.

Solid Casein Adhesive.—The mass, consisting of a mixture of alkali tannate, casein, and water, is said to possess good adhesive properties. In the dried state it forms a somewhat hard and rather elastic mass, which is insoluble in water and various other liquids. It is prepared by pouring a cold or warm solution of tannic acid (bark extract) into a solution of milk of lime until precipitation ceases and the filtrate has an alkaline reaction. The precipitate is separated, and is dried at the ordinary temperature in a current of air. This calcium tannate is powdered and mixed with lime, unless an excess of this base is present already, the whole being next ground along with casein powder, sifted and stirred up with a sufficient quantity of water. According to the desired character and properties of the finished product, from 1 to 10 parts of casein are taken to each part of tannate. Casein is not precipitated on adding water, but the mixture forms a strongly adhesive mucilage which, when dry, becomes hard, tough, elastic, and insoluble in water, petroleum, carbon disulphide, and other liquids.

Casein Glue for Cardboard Boxes.—45 parts of dry casein powder are dissolved by degrees in 64 parts of water with continued stirring, 1 part of borax and rather more than 1 part of strong ammonia being added to the mixture, which is next heated nearly to boiling for some time, the mass being still kept stirred, and finally cooled. If the glue is too thick, it may be thinned with a little ammonia. A good casein glue can also be prepared from casein powder, magnesium chloride, and gelatinised starch.

Casein Solution.—A preparation, patented by the Casein Company of America, is made by precipitating casein with hydrochloric acid, and dissolving 1 part of the precipitate in 1 to 3 parts of water with an addition of 0·1 to 0·12 part of trisodium phosphate.

A solution of casein which may be useful for certain purposes may be prepared by dissolving the albuminoid in alcohol by the aid of an alkali hydroxide (soda or potash), neutralising the alkali with an acid and then adding formaldehyde (H. V. Dunham, Assignor to the Casein Company, America, U.S. patent 821,620, May 29, 1906).

Joining Casein Plates.—A. Scheel (German patent 293,510). The plates to be joined are coated while still moist and unhardened, with an intermediate layer of moistened casein powder, the whole being then warmed under heavy pressure, which renders the intermediate layer plastic and binding.

Soluble Casein Compound.—C. Revis, E. R. Bolton, and W. N. Bacon, London (English patent 24,662, November 6, 1911), have taken out a patent for a casein compound formed by mixing together 10 lb. of borax and 300 to 500 lb. of wet casein (curd), containing 25 to 30 per cent. of dry matter. The product forms a homogeneous liquid which, when sprayed by an atomiser into a chamber heated to a temperature much higher than that of boiling water, falls to the floor in the form of an extremely fine and light powder, which readily dissolves in water to form a mucilage. The proportions given yield about 100 lb. of powder, containing approximately 10 per cent. of borax.

Renken's Method of Using Glue.—One side of the article to be glued is treated with formaldehyde, the other coated with casein putty, and the two pressed together. Bottle labels and the like are moistened with formaldehyde, dried and coated with casein glue.

Glue Powder.—To prepare glue powder, casein is mixed with powdered slaked lime in suitable proportions, the mixture being stirred up with water for use. A very good cement or binder is obtained by mixing dry casein with levigated chalk, powdered slaked lime, and a solution of sodium silicate or borax.

Casein Glue.—A. Bernstein (French patent 370,940, 1906) prepares a substance with the properties of glue by mixing casein with metallic silicates in the colloidal state. With this object, the casein, either in skimmed milk or after separation therefrom, is dissolved in alkalies or alkali salts in the usual manner, and is then mixed with water-glass and some metallic compound with which the latter will react such as calcium chloride, barium chloride, or magnesium chloride in aqueous solution. The casein combines with the metal of the chloride, while double decomposition is set up between the chloride and the water-glass, forming alkali chloride and the silicate of the other metal. This product (*e.g.*, for instance, magnesium silicate) is insoluble, and would be precipitated in the absence of the casein, but in presence of that substance it assumes the colloidal form, similar to that of the casein solution, the mixture of the two augmenting the adhesive properties of the casein. The following proportions of the ingredients may be regarded as typical: 100 parts of casein are mixed with 600 of water and dissolved by the addition of 12 parts of carbonate of soda. To this solution are added 100 parts of a 10 per cent. solution of magnesium chloride and 80 parts of sodium silicate or potassium silicate, the whole being stirred continuously. The dried product swells up like ordinary glue in cold water, and dissolves in hot water.

A mixture of casein, rosin, and alkali was patented as a cement by C. and A. Bernstein (German patent 270,200, 1913).

C. Wittkowsky also patented the use of sodium silicate for this purpose (English patent 9070, 1905).

Casein Glue for Match-making.—Casein forms a good substitute for glue or dextrin in match-making, for the following reasons: It can be dissolved without heat, is neither hygroscopic nor inflammable, and can also be made waterproof by suitable treatment.

The preparation of the solution is simplified by using soda casein or water-soluble casein instead of the variety soluble in alkali. Water is heated to near boiling (190° F.), and the casein powder is shaken in and stirred.

Lehner's Casein Putties.—1. Fresh curd is boiled with water until it has become a ropy mass, and slaked lime and finely sifted wood ashes are stirred into the solution. The proportions are:—

Curd	100 parts.
Water	200 ,,
Slaked lime	25 ,,
Wood ashes	20 ,,

2. Another putty, suitable for stopping large holes in masonry or for pointing joints in brickwork, is compounded of:—

Casein	12 parts.
Slaked lime	50 ,,
Sea sand	50 ,,

3. *Casein Bind for Meerschaum.*—Casein is dissolved in alkali silicate, stirred quickly with finely-powdered calcined magnesia and used at once, since it very soon hardens. If meerschaum powder be added along with the magnesia, the resulting mass closely resembles real meerschaum, and can be used for making a substitute for the same. The meerschaum powder is obtained by pulverising and sifting the waste turnings and shavings of real meerschaum.

4. *Casein Putty with Good Keeping Properties.*—

Casein	200 parts.
Quick-lime	40 ,,
Camphor	1 ,,

These ingredients are powdered separately, intimately mixed, and packed in tightly closed glass vessels. For use, the powder is stirred up quickly with the necessary quantity of water and used at once.

5. *Casein Cement for Porcelain.*—Casein dissolves readily in alkali silicate, the solution forming one of the best possible cements for porcelain. It is prepared by shaking up 1 part of fresh casein with 3 parts of water-glass in a bottle until dissolved.

6. *Casein Cement for Glass.*—

Skim-milk cheese	100 parts.
Water	50 ,,
Slaked lime	20 ,,

The cheese is separated from the rind, cut up into small pieces, and rubbed down with water until a ropy, uniform mass is produced, into which the slaked lime is stirred as quickly as possible, the mass being used as soon as made. It will not only cement glass firmly to glass, but can also be used for fastening metal on glass, porcelain, and meerschaum (pipe mounts).

7. *Casein Cement for Metals.*—

Levigated quartz sand	10 parts
Casein	8 ,,

mixed with sufficient water to make a cream.

8. *Casein and Borax Cement.*—(*a*) Ten parts of casein and 5 of borax are stirred with water to a thick milk, which is used as glue. The mixture may also be used as an adhesive for the labels of wine bottles, since it does not become mouldy or loosen in damp cellars.

(*b*) If the above cement be coated over several times with gallnut extract when dry, it becomes waterproof, owing to the formation of an insoluble compound between the casein and the tannin.

Very strong waterproof fabrics, similar to those treated with rubber solution, can be obtained by dipping closely-woven cloth in a solution of casein and borax, allowing it to dry, and then dipping it in a solution of gallnuts.

(*c*) Borax is boiled in water, and the cold solution is poured over freshly precipitated casein, which it thereby dissolves to a clear, thick, and strongly adhesive mass that will keep indefinitely without decomposing.

This preparation applied to paper, leather, linen, or cotton cloth forms a handsome glossy coating, and on this account it is largely used as a varnish for cardboard boxes or leather fancy goods.

9. *Casein and Water-glass Cement for Glass and Porcelain.*—Casein, 10 parts, and water-glass, 60 parts, are mixed

together. It is applied as quickly as possible, the cemented articles being exposed to the air to dry.

10. *Casein-Soda Cement.*—Casein is precipitated from milk with vinegar, then washed and redissolved in a minimum quantity of caustic soda solution, the preparation being stored in well-closed bottles.

Washable Cement for Deal Boards.—

Casein	18 ozs.
Water	7 pints.
Ammonia	½ „
Quick-lime	9 ozs.

Wenk's Casein Cement.—The casein is not used direct, but is first treated, so that after the addition of some colloidal substance with which it forms a complex (*e.g.*, tannin), it acquires superior properties to those of cements prepared in the usual way. The casein is rendered slightly alkaline with soda or potash, and then heated for about twenty-four hours at a temperature of about 140° F. It is next mixed with lime or water-glass, and finally with some material containing tannin, in order to ensure more rapid gelatination. The best results are obtained when the casein has been prepared at the above-named temperature; otherwise, it behaves less favourably. The tannin solutions to use are preferably about 1 per cent. of gallic acid, cutch, quercitannic acid, or similar substances. The slaked lime, water-glass, etc., which may be used in varying proportions, furnish the requisite inorganic solvents for bringing about the more intimate combination of the two colloids. The finished preparation may be used for gluing wood in the ordinary way.

Casein and Lime Cement.—The rind is removed from old, skim-milk cheese, and the mass is rubbed with water and warmed until it furnishes a viscid mass like honey. This mixture is next incorporated to a plastic mass with a sufficient amount of powdered, slaked lime, in a warm mortar. An alternative method is to take skim-milk curd, press out the whey, and mix the rest with lime as in the previous example. The cement must be used at once as it soon hardens. The curd will not take up more than one-fourth its own weight of lime. If larger quantities are needed, a little fine sand or brickdust, previously made up into a paste with the lime and a little water, may be used to replace part of the curd. When the cement is to be used in very fine joints, it is preferable to employ a solution of carbonate of potash as the solvent, and evaporate any superfluous water, or mix the fresh curd with the dry salt. This cement is particularly suitable for mending glass or porcelain.

"*Pitch Barm.*"—This is a cement capable of numerous applications, and is made by mixing fresh curd with water-glass and powdered caustic lime. The curd must be well pressed to expel the water and is then incorporated with the water-glass, the lime being stirred in so as to form a paste just before use. It hardens quickly.

Casein Stopping.—This is used for stopping cracks and joints in wood, stone, and brickwork, and is prepared by mixing 1½ parts of water-soluble casein, 8 of levigated chalk, 2 of calcined magnesia, and 2 parts of fine sawdust. Just before use the mass is stirred to a pulp with water. It penetrates the cracks, hardens quickly, smoothens nicely and does not shrink.

Casein Cement for Stone.—Fresh curd, pressed to expel the whey, is kneaded in warm water with about one-fourth its weight of powdered slaked lime, to form a soft, plastic mass which must be used immediately as it hardens quickly. To give the cement more body—which is desirable for use with stone—the lime should have been mixed beforehand with about its own weight of fine sand or brickdust, the mass being made up to a stiff mortar with water before adding the curd. The surfaces to be cemented must be well moistened.

Another excellent cement for this purpose, which sets slowly, becomes very hard, and answers admirably for protecting joints in stonework from water, alkalies, etc., consists of fine cement mixed to a stiff paste with one-fourth its own weight of fine brickdust, and with moistened curd.

A good cement for wood is made of equal quantities of powdered quick-lime, dry curd, and albumen, mixed together by stirring.

Insoluble Casein.—Morin makes an insoluble casein by treating the commercial article, preferably in the form of powder, with trioxymethylene, previously dissolved or suspended in water. The mixture is then heated to about 60° C., the casein softening to a pasty mass which can be shaped or moulded as desired. Under the influence of the small quantity of water which remains in the mass after pressing, the trioxymethylene is decomposed into formaldehyde, which substance, being in intimate association with the casein, renders the latter insoluble. This reaction proceeds slowly, so that no bubbles are formed. The mass may be incorporated with emery or the like, to form grindstones, or may be coloured in any desired way.

CHAPTER VIII.

THE PREPARATION OF PLASTIC MASSES FROM CASEIN.

Casein, like all substances possessing strong adhesive properties, is specially adapted for the preparation of plastic masses, which can be moulded, either alone in the form of paste or a more or less dry powder, or in admixture with organic substances like sawdust, wood meal, paper, etc., which masses can be readily moulded and set hard when dry. Casein mixed with lime or other alkaline material can be converted, by the addition of a little water, into a plastic mass which can be stained any colour, and dries, though very gradually, in the air to a transparent solid as hard as bone. In this condition it can be turned in the lathe or worked with ordinary cutting or carving tools. When plastic casein is mixed with other substances, such as organic or finely powdered inorganic materials, the resulting products dry much more rapidly, especially under the influence of warmth. Care must, however, be taken in the drying process—which should be slow—owing to the fact that all masses containing much water shrink and easily crack during the process.

The adhesive properties of casein, which have been adverted to in a previous chapter, have already met with extensive industrial application. Great success has also attended its application to render celluloid uninflammable; and special mention will be made later of the most recent celluloid substitute—galalith. This is an excellent example of how modern ingenuity has enabled a raw material, hitherto of but slight use technically, to become of considerable industrial importance.

Imitation Ivory.—Milk curd, partly or wholly freed from its aqueous and fatty constituents and broken up into small lumps, is kneaded for about fifteen minutes in water which is nearly boiling. This treatment causes the separation of fatty or granular impurities, leaving the casein in an almost perfectly pure state as a tough sticky mass. Care must be taken, however, not to prolong the kneading beyond the proper stage, or the curd will be too soft and weak. The product may after this treatment be pressed out into flat cakes or blocks of any desired shape.

The casein prepared in this way can be mixed with pigments or other materials, such as ivory dust, ground bone or ground porcelain, according to the character of the material it is intended to imitate. The prepared casein is stirred for about ten minutes in hot water, which causes it to soften; and it can then be incorporated with the necessary colouring matter or other ingredients, and the resulting plastic mass cast into moulds.

The curd, freed from whey, may also be kneaded in its own water of saturation, little more being added if necessary, at a temperature approaching the boiling-point. For this purpose, the curd should be broken into small pieces, this treatment facilitating the removal of fatty and other extraneous matter. By this means, the curd can be manipulated at a lower temperature and far more cheaply than by the first-named method, and also furnishes a tougher quality of casein. The colouring matters or other admixtures can be incorporated as soon as the fat has been washed out and the mass has been worked, thus obviating any special mixing process. The temperature to which the curd containing the water of saturation is exposed, should be about 120° to 175° F., according to the character of the curd. It is then worked or kneaded for about fifteen minutes, with or without the addition of a little more water, according to requirements, the water of saturation usually sufficing to render the mass plastic. The product being a tough, sticky mass which can be pressed into flat cakes or any other suitable shape. The preparation is specially adapted for various decorative or useful articles; the further treatment consisting in rolling, pressing, moulding, or any other suitable process.

Lilienthal's Plastic Mass.—The ingredients of this preparation consist of caustic strontia, powdered marble or limestone, and casein, the following proportions being recommended: powdered marble or limestone, 3 to 4 parts; caustic strontia, 1 part; and a quantity of pressed casein equal to about one-sixth of the other two substances combined. The ingredients are mixed together in any suitable mixing or stirring machine, the strontia and casein combining to form a very firm binder which imparts great hardness and strength to the articles made from the mixture. The mass is formed into the desired shape by moulding under heavy pressure.

Jung, Brecher & Kittel's Insulating Preparation.—This preparation is made of a mixture of casein and vegetable oils, which latter may be either in a natural state or sulphonated. The low price of rape oil, linseed oil, and castor oil renders them specially suitable for the purpose. The casein may be prepared in any suitable way, and is used either in the state of dry powder, the pressed damp condition, or dissolved in alkali, borax, or other solvent. In the two former cases the oil is kneaded with it until a homogeneous, gelatinous mass is formed, but when dissolved casein is used the liquid is evaporated until a kneadable mass is formed, which is then mixed with the oil.

The preparation may be worked up alone or in admixture with caoutchouc solution or rosin, to form a homogeneous mass, and when rosin is used the product may serve as a rubber substitute. It may be further incorporated with other ingredients used in the rubber industry, such as litharge, chalk, lime, pitch, or other colouring material. The final product is employed in the manufacture of imitation rubber goods by moulding and drying, and it may also be vulcanised with sulphur, irrespective of whether raw or sulphonated oil has been used.

Anti-Radiation and Anti-Corrosive Composition.—To prevent loss of heat by radiation from steam pipes, these may be coated with one or two layers of a mixture of 10 parts of casein and 25 parts of Portland cement and water-glass, the whole being stirred together and thinned to a workable consistency with water. Asbestos may also form part of the composition, or the pipes may be wrapped with asbestos rope before the second coating has dried. On account of its constitution and consistency, the composition may be regarded as a plastic mass rather than as a paint.

Dickmann's Covering for Floors and Walls.—In this invention paper, peat, or other vegetable or animal fibres, or cellulose, asbestos and the like, may be rolled into sheets or converted into a pulp in admixture with oxidised linseed oil, metallic oxides, casein dissolved in ammonia, alum, iron sulphate, water-glass, resins, paraffin, wax, salt, glue, gelatine, potassium chromate, rubber, flour, cuprammonium hydroxide, formaldehyde, or mixtures of two or more of these substances. The under side of the sheets may be fitted with projections; or holes or hollow cavities or cells can be arranged inside the sheet. These spaces may be filled with peat, sawdust, rubber, cork, linoleum, leather, or other sound-deadening material that is elastic and non-conducting; or compressed-air chambers may be provided within the material. Wall coverings of this kind may be decorated in any suitable way on the outer surface.

Imitation Linoleum.—Albumen, 50 to 80 parts; casein, 50; ground cork or leather scraps, 20 to 40; flowers of sulphur, 2 to 4; and caustic soda lye, 15 to 16 parts, are intimately mixed together to form a mass which can be rolled into strips. The main components are alkali albuminate and alkali caseate.

Imitation Leather.—Imitation leather may be produced from casein by preparing a felted mass of vegetable fibres and animal wool; this felt being impregnated with a mixture of linseed oil, rosin, turpentine, wax, glycerine, glue, and casein, together with small quantities of borax and potassium bichromate, the liquid having been gently warmed before use. After impregnation the felt is partly dried, and is then treated with a solution of aluminium acetate, followed by completing the drying process, cleaning and pressing between warm rollers. The product forms a very good imitation of leather.

Imitation Bone.—Clean, white bones or bone chippings are finely ground and mixed to a stiff paste with casein solution, which is then pressed in iron moulds and dried at 130° to 140° F. The mass is next roughly ground, moistened and dried under heavy pressure and at a high temperature in moulds. Steam presses are used, the size of the press and the working pressure varying with the dimensions of the plates to be produced; two men are required, one to look after the engine, the other in charge of the press. The metal moulds in which the plates are formed are heated in the press by means of the bed and pressing head, which are traversed by channels containing gas jets.

Artificial Horn, etc., from Casein.—C. Pozzi and A. Tondell (French patent 386,011, January 7, 1908) propose to treat skim milk with rennet at a blood heat, leaving it to stand ten to fifteen minutes when curdled, and expelling the whey by the aid of beaters. After standing half an hour the whey is poured off and the curd drained on a sloping table, washed with water, squeezed to remove fat and sugar, and bleached by washing with very weak sulphuric acid, hydrochloric acid, or other suitable agent, the surplus acid being removed by washing with lukewarm water. The next step is to heat the curd in a jacketed pan with twice its own weight of water, containing sufficient lactic acid to replace that naturally present in the whey, the temperature being slowly raised to 35° to 40° C. to facilitate the ripening of the paste. The desired stage will have been reached (in fifteen to eighteen hours) when a sample, plunged into boiling water, changes to a tough, springy mass, whereupon the temperature of the water jacket is raised to 70° to 75° C., and the contents of the pan are stirred with a spatula until they unite to a compact, tenacious, and fibrous mass. This is taken out of the pan and kneaded and rolled, at a constant temperature of 50° to 55° C., until all the water is removed. After cooling to 15° to 22° C., the mass is chopped small in a machine and transferred to press moulds or frames, in which it is subjected to pressure for twelve to fourteen hours. The pressed sheets are then stained to resemble horn, ivory, mother-of-pearl, etc., either plain or in fancy patterns, after which treatment they are spread out, one above another, on thick sheets of cloth in an iron frame, and placed in an autoclave charged with water containing glycerine and formaldehyde in different proportions, according to whether the product is desired to be more or less waterproof, flexible, or hard, the operation of endosmosis being accelerated by pumping air into the closed vessel until the pressure attains about two atmospheres. Here the sheets remain for about ten hours, and, after being dried, are ready for use.

By regulating the gas flames the heating can be adjusted and kept uniform ; on no account should the metal be heated to redness. The temperature is regulated by the melting-point of metallic alloys. The mould and cover are placed empty in the press and heated; and the interior of the mould being carefully greased or oiled, the necessary quantity of material is inserted, the cover put on and the pressure gradually applied. The press attendant requires to be skilled, in order to judge correctly when to stop pressing and take the plate out of the mould. When sufficiently pressed, the plates are removed into a moderately warm room to complete the drying.

The finished mass is very hard and tough; so much so that it will not break when thrown down on a stone floor. It can be turned in the lathe, like real bone, takes a beautiful polish, and is capable of numerous applications.

According to the "Eborit. Ges. m. b. H." (German patent 191,125, December 16, 1902), casein treated with dilute hydrochloric acid forms a gelatinous plastic mass which may be used for moulding purposes.

Plastic Mass of Keratin and Casein.—Substances containing keratin are dissolved in alkalies or alkali sulphides, together with casein, colouring matters, and the like. The keratin is thrown down from the solution by mineral acids and tannic acid, and the resulting mass is put into moulds, pressed and dried.

Insulating Mass.—This mass consists of a mixture of skim-milk casein and a solution of resins (preferably mastic or sandarach, with a little amber) in alcohol or turps (German patent 106,466).

Plastic Casein Masses.—Dissolved casein is mixed with a solution of resin, the mixture being incorporated with vegetable or mineral ingredients, and treated with formalin to coagulate the casein. This mass, whilst still in a plastic state, may be spread on a network of wire, rushes, or straw, so as to obtain a light, unbreakable, insulating material.

A. Bartels, Harburg, Germany (French patent 420,543, September 19, 1910), also claimed the production of horn-like masses by heating with water under pressure and then hardening with formaldehyde. A further patent granted to Bartels (U.S. patent 1,211,526, January 9, 1917), claims the use of a solution of hexamethylene tetramine and glycerine in the production of horny substances.

H. Morin (French patent 388,441, May 30, 1907), incorporates with the casein some trioxymethylene, which decomposes slowly with formation of formaldehyde, the casein being thus hardened, rendered insoluble, and also preserved from decomposition.

Substitutes for horn, ivory, and the like, are prepared, according to W. Plinatus (French patent 465,048, November 18, 1913), by treating casein, or albumen, or derivatives of the same, *e.g.*, alkali-albuminates with the acid or neutral esters of the higher alcohols or amino-fatty acids. By this treatment the albuminous compound becomes hardened or coagulated, and in this state may be mixed with other products to form plastic masses which may resemble horn, ivory, etc., according to the nature of the latter.

Plastic masses are also formed by mixing together albuminous substances in alkaline or other solution, casein, sodium carbonate, rosin oil, gum, and glue. The product is then moulded, dried, and afterwards steeped in formaldehyde. " Soc. anon. franc. de Chim. Ind." (French patent 425,204, March 30, 1910).

The " Soc. anon. L'Oyonnaxienne " (French patent 472,192) claim the use of mixtures of casein with amines, amides, and their derivatives, as, for instance, aniline, acetanilide, etc., for the formation of plastic masses.

In the manufacture of a thermoplastic material from casein, B. B. Goldsmith, New York (U.S. patent 840,931, January 8, 1905; English patent 14,098, June 18, 1907), mixes with it β-naphthol and submits the material to heat and pressure.

According to another process, milk is warmed to about 140° F., treated with a considerable addition of borax, and heated further to about 190° F. in presence of barium chloride or other mineral precipitant of casein. The washed precipitate is pressed and ground with an addition of acetic acid, soda or other solvent, and the resulting mass is put into a steam-heated press. The product is similar to bone or celluloid.

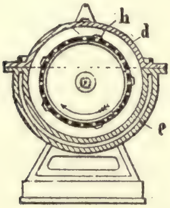

FIG. 15.

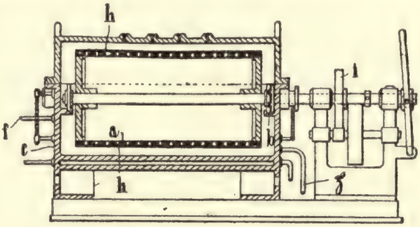

FIG. 16.

Manufacture of Transparent Horn-like Casein Masses.—No. 13,203 of 1916.—Dr. A. Bartels, of No. 102 Buxtehuderstrasse, Harburg an der Elbe, Germany, claims: (1) A process for the manufacture of transparent horn-like casein masses which consists in agitating dry commercial casein with a fat solvent for a considerable time at a temperature above that of the atmosphere, and after drying, treating the product in the usual manner. (2) A process as claimed according to claim 1, wherein alcohol or a mixture of alcohol and benzol or benzine is employed as the fat solvent. (3) A process as claimed in claim 1, wherein the dry commercial casein is agitated in a rotating extracting vessel with a fat solvent, the latter being renewed if required, whereupon, after running off the extracting agent, the casein is heated in the same rotating vessel in a vacuum with energetic motion for the purpose of being dried, after which it is worked up into artificial masses in the usual manner. (4) An apparatus for the carrying out of the process specified in claims 1-3, having a strainer drum which serves to hold the material to be treated and which is rotatably mounted in a liquid-containing cylinder in such a manner that, as the strainer drum rotates, the liquid solvent admitted into the cylinder is carried up and distributed thoroughly over the whole material in movement, characterised in this, that the liquid containing cylinder is divided longitudinally, and that the upper part is removable. (5) An apparatus as claimed in claim 4, wherein the strainer drum is provided in its periphery with scooping channels for the purpose of carrying up large quantities of the liquid solvent in its rotation. (6) An apparatus as claimed in claim 4, wherein the drum shaft is divided and provided with a coupling so as to allow of lifting the strainer drum out of the casing, and also wherein one wall of the drum is made wholly or partly removable, or is adapted to be opened for the purpose of charging and discharging the contents of the drum.

Horny Casein Mass.—According to P. Horn, dried casein is dissolved in dilute caustic potash, and heated along with a quantity of sulphur at least equal to the amount of alkali taken. The casein, potash, and sulphur are thereby dissolved to a clear liquid, which is concentrated to the thickness of syrup, moulded and dried, or made suitable for various technical purposes by the addition of loading ingredients, driers, or hardening preparations. For example, a very elastic mass is obtained from the following proportions :—

Water	200	parts by weight.
Casein	100	,, ,,
Potash	5 to 10	,, ,,
Sulphur	10 to 30	,, ,,

The elasticity increases with the proportion of sulphur taken. The final product may be hardened by adding lead hydroxide, zinc hydroxide, and potassium or sodium silicate, whilst wood, cork, sand, or emery may be added to increase the drying properties, or as fillers.

In another recipe, 100 parts of skim milk are treated with about ½ part of acid, sulphuric, or hydrochloric. The precipitated casein is separated from the liquid, and set aside for one to three days to ferment, whereupon it is pressed, and dried at 140° F. The mass is powdered, and 70 parts of it are mixed with 28 of bone meal, gypsum, kaolin, or graphite, together with 2 parts of stearin, paraffin, wax, etc., and colouring matter if necessary. The whole is made into a pulp and warmed at 190° F., moulded and pressed, the finished product being dusted over with calcined magnesia, immersed in water for two days, and finally dried at 68° F.

Production of Plastic Masses from Casein.—To obviate the necessity for employing acids in the preparation of plastic masses from casein, Kathe (English patent, 17,953, August 7, 1907) merely heats the casein with water to a high temperature, at which the former undergoes a change of character. The amount of water the casein will absorb varies slightly according to the degree of purity of the material itself, but is independent of the quantity of water employed for heating. Thus, if 1 part of casein be heated with 10 parts of water, the resultant plastic mass is the same as if the proportions were only two to one. The granular casein changes into a coagulated, coherent mass, similar to caoutchouc, from which all the water that is not chemically combined can be removed, leaving a soft, uniform substance, which, on compression and cooling, furnishes articles of considerable hardness, needing only a few days' drying. The casein may also be mixed with the necessary amount of water, and heated in moulds with superheated steam.

J. Kathe, Cologne, declares his invention as described in the following statement: In the production of plastic masses from casein according to the German patent, 147,994, the disadvantage arises that the plasticity of the casein cannot be attained either by damping or by the use of great pressure and heat, so that a process is claimed in which use is made of small quantities of acids. The present invention consists in that the use of chemicals is wholly abolished, and a mass with greater plasticity is obtained by simply treating the casein with water vapour whereby an agglomeration of the casein takes place. The amount of water vapour absorbed by the casein is dependent upon the purity of the casein. By this treatment the granular casein is converted into a rubber-like mass from which all the water, which has not combined therewith, but is only mechanically enclosed, can be removed. There then remains a soft mass, which in this condition is pressed producing fairly hard objects which require only a few days wherein to dry. In order to render the material less pervious to water, the pressed objects are treated with formic aldehyde.

K. P. Boerma (German patent 241,887, January 16, 1910), also uses water only for rendering the material workable; the casein after moistening, containing 20 to 42 per cent. of water, is heated under high pressure whereby it is converted into a homogeneous mass which can be moulded into any form required.

Plastic Mass from Celluloid.—The inflammability of celluloid can be diminished by the addition of incombustible substances, of which casein is one; and this application of casein has already been repeatedly advocated and employed.

According to H. V. Dunham, Assignor to the Casein Company, New York (U.S. patent 748,709, January 5, 1904), a product resembling celluloid can be obtained by mixing solutions of casein and nitrocellulose in glacial acetic acid or other known solvents, with camphor or the like material used in the manufacture of celluloid.

To obtain a homogeneous compound of nitrocellulose and casein, Barnodai converts casein into a plastic mass by means of an aqueous solution of borax or other casein solvent, removes the excess of water, dips the product in alcohol in order to displace a portion of the water absorbed by the casein, eliminates the excess of liquid, and then introduces into the mass a quantity of elastic nitrocellulose, the whole being kneaded until homogeneous.

According to the Compagnie Française à Celluloïd, a cheap substitute for celluloid is obtained by introducing casein into the composition from which celluloid is prepared. One hundred parts of casein are moistened with a solution of 5 parts of urea in 50 parts of denatured alcohol, and mixed, after forty-eight hours, with nitrocellulose and camphor moistened with alcohol. After a further forty-eight hours the mass is treated in the same way as celluloid paste, with the subsequent addition of formaldehyde to render the casein insoluble.

Casein-Cellulose Composition.—A composition suitable for many purposes forming also an excellent electrical insulator and waterproof material when subjected to heavy pressure, can be prepared from cellulose and an ammoniacal solution of casein. If necessary the mass may be incorporated with repulped paper with or without the addition of a mineral substance such as magnesia, talc, kieselguhr and some body colour. The casein may be replaced by pressed curd, and the waste paper by alkali cellulose (J. G. Jurgens and H. Timpke, French patent 420,164, 1890). In the latter event, the alkali in the cellulose dissolves the casein, which thereupon penetrates into the cellulose furnishing a homogeneous product which can be incorporated with vegetable fibres or powdered mineral substances and coloured with pigments. The product may be made more impervious to water by adding to it a solution of ferrous sulphate or copper sulphate, or an alkaline solution of shellac, mixing the whole well and pressing it in metal moulds. The finished articles can be worked in the same way as wood.

Fireproof Cellulose Substitute.—A hard, glossy fireproof substance is obtained by the following recipe. A solution of 200 parts of casein in 50 parts of strong ammonia and 400 of water is mixed with—

Quick-lime	240 parts
Aluminium acetate	150 ,,
Alum	50 ,,
Gypsum	1200 ,,

followed by 100 parts of linseed oil.

The mass is kneaded until perfectly homogeneous, and is then rolled into sheets of any desired thickness. These are dried and pressed in hot metal moulds, or else are reduced to powder, filled into moulds and exposed to heavy pressure. The moulded articles are dipped into a bath of 10 parts of phosphoric acid in 100 of water, and are afterwards dried, polished, and varnished with a solution of shellac, consisting of 3 parts of shellac, 1 of borax, and 20 of boiling water.

According to another recipe, plastic articles of all kinds, and especially decorations and ornaments of paper, can be made to appear as though made of plaster of Paris, stamped sheet metal, or carved wood. Two press moulds are used: one positive, the other negative, fitting accurately one into the other. A few sheets of ordinary paper, previously moistened, are laid in the negative mould and worked with the finger tips so as to fill up all the depressions in the mould. Casein glue is applied to each sheet before the next is put in; and when a sufficient thickness has been attained (14 to 15 pieces of ordinary packing paper are usually enough), the positive mould is placed in position and the whole subjected to heavy pressure in a press. By this means the wet paper is forced into all the edges, projections, and depressions of the negative mould, and when the former is taken out of the mould it will be found that all the outlines and other details of the negative mould have been sharply reproduced on the surface. The paper is then dried, and at the same time exposed to the action of formaldehyde vapour. Finally, the ragged edges are trimmed, and the finished article can be coloured or gilded as required.

Franquet's Celluloid Substitute.—Celluloid and xylonite, both of which are used to make imitation tortoiseshell, ivory, horn, etc., are expensive, and the casein products, such as lactite and lactoite, are frequently brittle, or become so in time. According to Franquet, however, the product obtained by mixing casein with nitrocellulose and camphor, possesses the same properties as celluloid, and is much cheaper. It is flexible, very hard, without being brittle, and is impervious to water; it can also be sawn, turned, filed, and carved. When heated to 160° to 190° F. it becomes very plastic and can be moulded.

To obtain a homogeneous compound of nitrocellulose and casein, the latter is formed into a plastic mass with one of its solvents, *e.g.*, an aqueous solution of borax; the excess of water is removed, the mass is dipped in alcohol, to extract a portion of the water absorbed by the casein, the excess of liquid is removed from the mass, and the latter is then kneaded along with plastic nitrocellulose until homogeneous.

When camphor is used, 100 parts of nitrocellulose are treated with 40 to 50 parts of camphor dissolved in 50 to 60 parts of 95 to 96 per cent. alcohol. The casein is rendered plastic in the following manner: The casein is immersed for twenty-four to forty hours in a 5 per cent. aqueous solution of borax, or other casein solvent, *e.g.*, sodium carbonate. It is next dried, dipped in alcohol, acetone, sulphuric ether, or acetic acid, dried for several hours or pressed, and mixed with the nitrocellulose. Another method is to steep the casein for twenty-four to forty-eight hours in borax solution, or in some other casein solvent containing 3 to 4 parts of alcohol or other solvent of nitrocellulose. The casein and nitrocellulose products are afterwards rolled together for three to four hours between rollers, and thus furnish a transparent or translucent and perfectly homogeneous mass, which can be drawn out into sheets 2 to 4 inches thick. These sheets are pressed together, as in making celluloid, the block being thereupon cut into plates of the desired thickness. Mineral and other substances can be easily added to the mass. According to an additional patent (February 23, 1902) casein alkali compounds are added to nitrocellulose that has been treated with alcoholic camphor, the mixture being then treated in the same way as celluloid.

According to the master patent (German patent 138,783), a mass resembling celluloid is obtained by adding casein to ordinary celluloid; and pure casein may be replaced, for this purpose, by a compound of casein with a metallic oxide. For a transparent product, the casein-aluminium compound is the most suitable adjunct; the zinc or magnesium compounds for a white product, and the corresponding compound of manganese, iron, copper, or nickel for coloured articles. The casein compound must be repeatedly and carefully washed, from 1 to 5 per cent. of borax being added towards the end of the process, to render the mass more plastic and facilitate mixing with the other ingredients.

Plastic Mass with a Casein Basis.—Jannin claims for the plastic mass prepared in the following manner that it will replace celluloid and caoutchouc for many purposes, being very solid, and at the same time easy to cut, saw, turn, and work in various ways without splitting or cracking, besides being uninflammable, a good electrical insulator, and capable of resisting the action of chemical reagents. In principle, the method consists in mixing casein with some fibrous material like cotton or wool cut into short lengths, in order to render the casein less brittle and enable it to be worked without splitting, the proportion of fibrous material used varying according to the degree of strength and translucency or opacity desired. A certain quantity of oil or other fatty matter, glycerine, etc., is also desirable, but not essential. The following proportions may be regarded as typical: Water, 100 parts; alkali, 5; fibrous material, 10 to 50; oil or fatty matter, 10; casein, 100; colour, *quant. suff.* The water and alkali are mixed, and the colouring matter incorporated. The finely divided fibrous material is then stirred in, followed by the oil and casein in succession, the mixture being stirred and heated to dissolve the latter. The pasty mass is rolled to complete the mixing and expel imprisoned air, after which it is moulded into blocks, rolled into sheets or formed into any desired shape. Formalin or other hardening agent may be added.

F. von Kagenek (German patent 281,541, November 12, 1913) has patented a combination of casein and gelatin, which is treated with sodium silicate to render it plastic, and is then hardened by the addition of alum. This is stated to be suitable as a substitute for celluloid.

In the process invented by L. Collardon (French patent 359,073, November 2, 1905), casein is incorporated with a 20 per cent. solution of viscose (cellulose thiocarbonate) or other cellulose derivative, together with a solvent at a temperature of 60° C. This forms a plastic mass which may be moulded. Substances which decompose the viscose and at the same time render the casein insoluble, and thus harden the composition, may be at the same time added.

Galalith.—Galalith is the name applied to a plastic mass which, in a variety of forms and colours, has found a large number of practical applications. The method of preparation is based on the production of a clear, non-milky casein, first disclosed in the German patent 115,681, granted July 15, 1899, to Adolf Spitteler of Prien, Upper Bavaria.

The specification of this patent states that the cheap, imperfectly purified, commercial varieties of casein furnish turbid solutions, which in turn yield translucent, but not transparent, solid products. True, according to Lundberg, casein itself, when in the form of faintly alkaline solutions, is soon transformed into alkali albuminate ; nevertheless, these solutions will remain milky, both when heated and when kept for several days, if impure casein has been used ; neither can they be clarified by repeated filtration. If such solutions be precipitated, the substances causing the turbidity are thrown down as well, the deposit when dried being opaque, in thick layers.

It has been observed, however, that caustic alkalies precipitate these opaque substances, thus enabling clear solutions of casein to be obtained.

Technical casein is mixed with 13 times its weight of water, containing in solution 2½ parts of Na_2O per 100 of dry casein. This gives a uniform milky liquid, which when treated with progressively increasing quantities of 5 per cent. caustic soda furnishes the results expressed in the following table. No further change is produced by even doubling the quantity of caustic soda, though the addition of larger proportions of 20 per cent. soda lye cause precipitation of a sodium casein product, which redissolves on dilution with water.

The action of caustic alkalies differs considerably according to the quantity employed. Several times the amount of alkali necessary for solution may be added without any very appreciable change being produced, the solution merely becoming somewhat thinner. On the other hand, if the addition of caustic lye be continued, the liquid commences to thicken, and finally separation is effected into a perfectly clear solution, containing the casein, whilst the opaque particles are deposited in the form of a sediment.

Total Percentage of Caustic Soda Referred to the Dry Casein.	Behaviour of the Casein Solution.	Total Percentage of Caustic Soda Referred to the Dry Casein.	Behaviour of the Casein Solution.	Additional Remarks.
2½ °/o	Fairly thin, grey, opaque, homogeneous solution.	12 °/o	Gelatinous, faintly greenish, perfectly homogeneous, translucent with the appearance of boiled starch.	
3½ °/o	Somewhat thinner than the foregoing.			
4½ °/o	Do. do.	13 °/o	Thinner jelly.	A sample, shaken up with cold water, separated into liquid and sediment.
5 °/o	Do. do.			
6 °/o	Do. do.			
7 °/o	Do. do.			
8 °/o	Do. do.			
9 °/o	Do. do.			
10 °/o	Whiter in colour, signs of thickening.			
11 °/o	Thick jelly.	14 °/o	Perfectly water-white solution separated from very voluminous, muddy, whitish precipitate.	
11 °/o	A sample turned green like whey on boiling, and when left to stand, separated into an imperfectly clear liquid and a sediment.			

Further experiments have shown that heat, concentrating the solution, and prolonged standing, all favour the separation, which, moreover, can be effected very quickly by a single addition of alkali. Casein solutions prepared without alkali, and even milk itself, can be converted in this manner into a clear solution and a precipitate. The resulting clear liquid is colourless, greenish-yellow, brownish, or red, according to the purity of the casein and to the temperature employed.

Since the various technical varieties of casein exhibit different conditions in solution, in consequence of the methods of preparation adopted, it is impossible to state a minimum quantity of alkali that will cause separation in all cases ; a preliminary test will, however, furnish the necessary information.

The clear casein solutions prepared in the foregoing manner can be treated—after removal of the sediment—in the same way as the turbid solutions. For instance, the casein may be precipitated by an acid, and used in place of ordinary casein, or the precipitate may be dried—whereby it becomes perfectly transparent—and worked up into artificial amber, jet, etc.

The claim advanced for the method is for the preparation of transparent masses by treating casein, either dissolved or suspended in water, with sufficient excess of caustic alkali to precipitate the opaque particles, the casein being retained in clear solution, from which, after removal of the sediment, the casein can be precipitated and worked up in any suitable way.

In a further patent (141,309, March 5, 1902) it is claimed that the caustic alkali originally prescribed can be partly or wholly replaced by alkali carbonates, further experiments having shown that these carbonates have also a clarifying effect when added in quantities larger than is needed to dissolve free casein. The resulting clarification is not so complete as when caustic alkali is used, the latter, however, acting also on the sulphur compounds present in the casein solution, causing a yellow discoloration of the clarified solution or of the precipitated casein, unless the operation be performed with extreme care. Hence when a colourless product is specially desired, the caustic alkalies may be advantageously replaced, wholly or in part, by the corresponding carbonates.

For example, 55 gallons of milk, separated from impurities as far as could be effected by repeated treatment in a centrifugal machine, were treated with 7¾ lb. of soda (equal to about 40 per cent. of the weight of casein content). After a short time the colour changed, and on passing the liquid again through the separator, a greasy, muddy sediment was eliminated. The casein, precipitated from the resulting liquid by acids, was in thin sheets, colourless and transparent.

In German patent 147,994 (February 19, 1901) a process was described for imparting to dried casein the necessary plasticity to enable it to be moulded, this result being attained by moistening the casein with a little acid, *e.g.*, acetic acid, instead of water, before pressing.

When freshly precipitated from milk, casein is plastic and can be easily consolidated in moulds. On account of the large percentage of water in this fresh casein, however, the articles prepared from it are difficult to dry without warping and cracking; the casein itself being also very liable to decompose during the long period required. On the other hand, the use of the stable, dry casein is attended with the disadvantage that it loses its original plasticity in course of conversion into the commercial form, this plasticity not being recoverable by simply moistening the dry product; consequently, exceedingly high pressure and heat are required to form the same into a compact mass. As a result the colour and hardness of the article may be seriously affected by the heat.

The plasticity can, however, be restored by treating the casein with a trace of acid, preferably at the stage of moistening the mass before pressing. The degree of acidity most suitable varies, of course, with the different kinds of commercial caseins, but may be easily determined by trial. The acetic acid used for souring milk in dairies will do for the purpose very well.

To prepare a hard casein mass, casein, either in solution or in the dry, soluble state, is converted into the insoluble form by acids or salts, and treated with formaldehyde. It is advisable to free the casein from excess of water, by evaporation or pressure, before adding the formaldehyde.

The product obtained in this way, and known as galalith (from the Greek, *gala* = milk, and *lithos* = stone)—a name somewhat misleading since it cannot be regarded as petrified milk—has been adverted to by Dr. K. Hassack as follows: The horny fundamental mass can be converted into products of manifold colours and uses by the incorporation of pigments, earths, cellulose, ground cork, etc., with the casein previous to hardening it with formaldehyde. Imitation jet or ebony, for instance, can be prepared by adding 2 per cent. of lampblack and precipitating with lead acetate, preferably warm to secure a curd with less moisture. The precipitate is triturated with water, drained and carefully dried on a cloth strainer. Drying must proceed very slowly to prevent cracking, and, therefore, takes several months. The resulting dark grey cake is thoroughly soaked with formaldehyde, and when dried and polished exhibits a glossy, deep black colour. Other colours may be obtained by varying the pigment. Thus, nickel sulphate, used for throwing down the casein, gives a fine green mass, whilst copper sulphate yields a peculiar bluish green, and so on. Very good imitation marble is obtained by stirring mineral pigments with the freshly precipitated casein, and particularly novel effects are furnished by mixing bronze powders with the plain or coloured casein, before hardening with formaldehyde. The Gummiwaaren Fabriken (Rubber Works) of Harburg, Vienna, produced at their various factories, by the aid of pressure, sheets of galalith from $\frac{1}{12}$ inch thick upward. By means of special tubular presses they make galalith tubes and rods for turnery goods, knife handles, penholders, umbrella and stick handles, chessmen, cigar-holders and mouthpieces for same, small boxes, buttons, dominoes, card counters, inlays for cups, coloured furniture decorations to replace coloured glass. These and many other articles are now made of galalith in Vienna, Gablonz, and Nuremberg.

By pressing it in suitable moulds, galalith is also made up into backs for brushes, hairpins, rings, and fancy articles, and it is also made in sheets for cutting out combs of all kinds. As a rule the mass is pressed before treating it with formaldehyde, but for thin articles this procedure may be reversed.

Dr. Hassack and his assistant, Sudey, were engaged in making comparative tests with galalith and celluloid; and up to the present the following particulars are available. The two substances agree closely in specific gravity, that of galalith being 1·317 to 1·35, according to the admixtures present, whilst celluloid is 1·34 to 1·4. In point of hardness galalith is a little inferior to calc spar, namely, 2·5, whilst that of celluloid is below 2; and this substance can be scratched by gypsum. One important difference in the working qualities is that while celluloid can be easily cut with a knife, galalith is difficult to cut, and chips a good deal. With the saw or on the lathe they can both be worked readily, but galalith the less easily on account of its greater hardness. Both polish well, but galalith the better of the two, giving a higher gloss. Celluloid is more elastic, thin sheets and rods recovering their original shape at once when bent or rolled, whereas galalith sheets or rods are brittle when bent. Galalith also has the drawback that it cannot at present be produced in sheets less than about $\frac{1}{12}$ inch thick; and unlike celluloid, which can be obtained in transparent sheets as thin as paper, and in fine threads. Neither can the sheets be obtained perfectly clear like glass; nor is it so plastic as celluloid though it becomes soft, like horn, on prolonged soaking in boiling water. It gradually absorbs a considerable amount of water when soaked, *viz.*, according to experimental results, 30 per cent. in six days at room temperature, and 33 per cent. in twelve days, swelling and becoming like cheese, whereas celluloid absorbs barely 1 per cent. of moisture in the same time. Galalith is unacted on by fats, oils, benzol, ether, alcohol, or dilute acids, but it swells considerably in alkaline liquids, which have no action on celluloid.

Both materials are poor conductors of electricity. Thus experiments made in the Vienna Technical High School with plates of celluloid and of galalith $\frac{1}{12}$ inch thick showed both to be impervious to a current of 16,000 volts. The points of superiority possessed by galalith over celluloid are its freedom from smell and its uninflammable character. If held in a flame it merely chars, swelling up and giving off a disagreeable smell like burnt horn, whereas celluloid—as is well known—ignites at once and continues to burn rapidly with liberation of pungent vapours of camphor. The non-inflammability and insulating power of galalith will ensure its extended use in electrical work.

Galalith is made on a large scale at the Wimpassing and Harburg works of the above-named company. The casein is obtained from dairies in Hungary, Bohemia, and Moravia, where it is separated from sweet skim milk by rennet, the whey being consumed for fodder. Galalith factories are increasing in number in Europe. In 1910, at Lurgere (France), 440,000 lb. of casein were converted into galalith—the produce of thirty-five dairies which sent milk to the factory. It requires 15·85 gallons of milk to produce 2·2 lb. of galalith.[1]

A similar product to galalith is formed by heating casein

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[1] For the preparation and properties of galalith see G. Bonitt ("Zeitschr. angew. Chem.," 1914, **27**, 2).

with water under pressure and then hardening with formaldehyde ("Soc. anon. franc. de Chim. Ind.," French patent 425,204, 1910).

Insoluble Preparation of Casein.—Desgeorge and Lebriel, in making a supple, insoluble preparation of casein and other albuminoids, endeavour to overcome the defects of existing methods, using metallic oxides, acids, etc., by utilising the chemical activity of the electric current to increase the absorption of these oxides or acids by the casein, and consequently increase their effect. The casein is attached to the positive electrode of an electrolytic cell, charged with a bath consisting of water 1,000 parts, sulphuric acid 150 parts, and tannic acid 500 parts, the negative electrode being formed of a plate insoluble in the bath. The sulphuric acid supplies the casein with the sulphur, enabling it to absorb the oxygen of the bath, whilst the tannic acid increases the insolubility of the product and renders it supple and non-putrefactive. The current decomposes the bath, liberating hydrogen at the negative electrode, whilst the oxygen of the acids present flows to the positive pole, where it is absorbed by the casein. Harder products may be obtained by replacing 100 parts of the sulphuric acid in the bath by 50 parts of phosphoric or other acid. The tannic acid may be replaced by other insolubilising agents according to the uses for which the casein is intended.

The Treatment of Casein and other Albuminous Substances.—R. Desgeorge, Lyons, and F. Lebriel, Villeurbanne, claim: (1) A process for the treatment of albuminous substances for obtaining non-inflammable products in imitation of horn, shell, ivory, celluloid and the like, consisting in adding to said substances a solution of chloride of sodium, and submitting the product to an electrolytic treatment with the use of metallic electrodes. (2) The process as in claim 1, wherein electrodes of such nature are used as to impart colour to the finished product. (3) The process as in claim 1 or 2, wherein the electrolytic treatment is continued until complete insolubility of the product is produced.

The Condensation of Casein, Phenol, and Formaldehyde.—The condensation of phenol and formaldehyde in presence of acids or alkalies to form a solid, inert substance is the invention of Dr. Baekland; the product being well known in America under the name of "Baekelite". K. Albert and L. Berend (French patent 436,720, August 18, 1911) have taken out a patent in which condensation products of casein, phenol, and formaldehyde are formed. This invention consists in mixing together intimately 25 parts of casein, 25 parts of phenol and 2 parts of caustic soda. The mixture is heated until it forms a viscous homogeneous liquid; 50 parts more phenol and 10 parts of trioxymethylene are then added and the heating discontinued when the temperature has risen to 100° C. Further additions of 10 and 5 parts more of trioxymethylene are made at intervals with further heating until a sample removed solidifies on cooling. This product can be readily moulded and can be hardened by heating at 100° to 110° C. or for longer periods at lower temperatures. Other phenols may be used in place of ordinary phenol.

CHAPTER IX.

USES OF CASEIN IN THE TEXTILE INDUSTRY FOR FINISHING PURPOSES, COLOUR PRINTING, ETC.

CASEIN is used chiefly in calico printing, more rarely in the finishing department. The gummy ammoniacal solution of casein is employed as a medium for printing and fixing powdered pigments that are unaffected by alkali. Fairly well-fixed colours are obtained when the ammonia has been driven off by vigorous drying or steaming. Solutions of casein in lime-water can also be used in the same way; in this case the colours are fixed by the action of the air, the carbonic acid in which acts upon the compound of lime and casein, forming calcium carbonate and insoluble casein.

Pure casein is almost entirely insoluble in water, but, as already mentioned, it will dissolve in water containing carbonates, phosphates, alkalies or even alkali chlorides; weak alkali being the most efficient solvent. These solutions, in which the casein forms a weak compound with the alkali, differ from solutions of albumen inasmuch as they neither become turbid nor coagulate when heated. They, however, acquire this property after the addition of magnesium sulphate, and turbidity also appears in solutions of casein in lime-water, in which it is readily soluble. When casein solutions are treated with mineral acids, a flocculent curd is precipitated, which may consist of an adsorption compound of the casein with the added acid. A similar precipitate is produced by acetic acid, but is redissolved on adding an excess of hydrochloric acid, though reprecipitated on the amount of acid being still further increased.

Casein solutions are also precipitated by the action of the mucous membrane of the stomach of the calf (rennet), and also by the gastric juice of carnivorous animals. Precipitation is also brought about by tannic acid and metallic salts, indefinite compounds with which are formed, and parallel to the behaviour of alkaline solutions of casein we find natural solutions of the substance, such as milk, behave in a similar manner.

Caseogum, which is a solution of casein in lime-water, is used as an adhesive, more particularly for impregnating cotton and linen fabrics, and, on exposure to the air, absorbs carbon dioxide. The casein, deposited on the fibre, imparts to the latter greater affinity for dyestuffs.

Thirty-two parts of fresh curd are stirred with 48 parts of water at 64° F. and rubbed through a metal sieve in order to reduce it to a finer state of division. On the other hand, ¾ part of fresh, well-burned lime is slaked gradually with warm water until it falls to powder, which is thereupon mixed with 3½ parts of warm water, triturated, filtered through paper, and the solution added gradually to the curd by stirring. The mixture at first thickens, and it is only after prolonged stirring that it becomes thinner and attains the desired consistency. Care must be taken to have fresh lime of good quality, and to slake it with just the right quantity of water; neither too much nor too little. The curd must be rubbed down fine with the water so as to eradicate all lumps, and the water must be at the temperature already specified.

"*Glutin.*"—"Glutin" is a glaze for dressing curtain fabrics, also used as a medium for colours in dyeing and calico printing. It is prepared as follows:—

Curd, freed from adherent moisture by pressure, is ground to a coarse, uniform powder, between rollers revolving in opposite directions. This powder is mixed with a solution of 1 part of sodium tungstate, and again put through the rollers in order to crush the particles of curd as fine as possible. As soon as the solution is brought in contact with the perfectly dry curd, the reaction commences at once and the mass begins to grow tougher. Should the curd contain much buttermilk, it is stirred up with a little hydrochloric acid and water, and repeatedly washed with water until all trace of acidity has disappeared. This done, the curd is pressed again and used as above described.

The cold mixture containing the sodium tungstate is placed in a water-jacketed pan, mixed with a little water if too dry, and melted at a moderate temperature with constant stirring, until a sample no longer shows any unaltered curd. The mass may be preserved from putrefaction by adding a little carbolic acid or oil of cloves. When the mass is all melted, it may be poured out to cool, and then furnishes a more or less solid mass, according to the amount of water that has been added.

This material is soluble in water in all proportions, the mass possessing highly adhesive properties, and it is particularly useful for fastening paper labels on sheet metal. When once dry, it is fairly waterproof. Curtains printed with earthy or metallic colours and this preparation have a fine gloss, and the coating is rendered more flexible by the addition of glycerine. "Glutin" is also soluble in glycerine, forming therewith a fine, tough mass which, when applied to paper, gives a flexible coating that can be made as hard as leather by passing it through a solution of alum after drying.

Casein Dressing for Linen and Cotton Fabrics.—Four parts of casein are stirred with 30 of water, followed by a gradual addition of 1 part of lime that has been slaked to powder. At the same time, 2 parts of neutral soap are dissolved in 24 parts of water, this solution being added to the casein solution. The fabric is impregnated with this preparation, and afterwards passed through a solution of aluminium acetate, heated to 120° to 140° F., whereby the casein is rendered insoluble and is precipitated on the fibre along with the aluminium soap.

Argentine is the name applied by Heim to a special powder prepared by the action of metallic zinc upon a solution of a tin salt, and the combination of this powder with casein, as a dressing for yarns or fabrics, to impart to them a metallic finish.

The tin precipitate is obtained from a solution of "tin salt" (stannous chloride) by the aid of metallic zinc and the electric current; the powder, after drying, being passed through a gauze sieve, the coarse particles thus removed being redissolved for use again, while the fine powder is used in the preparation of the dressing.

The casein is prepared by moistening 1 part of casein powder with water and allowing to stand for six to eight hours, after which it is diluted with water containing strong ammonia equal to one-quarter the weight of the casein in which the latter swells to form a jelly which is diluted with more water till a fluid is formed into which the argentine is stirred. Should the material become thick on standing, the vessel containing it may be placed in a pan of water, which is heated, whereupon it becomes ready for use again immediately. To render the printing colour more workable it may also be mixed with a strong gum-arabic solution, preferably of a pale colour and well strained.

The casein solution may also be prepared in the following manner, according to whether it is to be used as a dressing for printing: 2½ parts of casein are softened for ten to twelve hours with 7 parts of lukewarm water containing ¾ part of strong ammonia. During this time the casein will have swollen up thoroughly, and can then be diluted with a further 7 parts of lukewarm water, after which acetic acid is added until a precipitate is no longer visible.

The most important point in making this argentine preparation is to have plenty of metal present, if the fabric is to exhibit a silvery lustre when calendered, since it must be remembered that the lustre is in nowise due to the medium, but solely to the properly amalgamated finely divided metal, under the influence of friction.

When printing colours or dressings become thick on standing, they must not be diluted with any preparation, but should be warmed in a pan of hot water or on a water bath.

Printing Colour with Metallic Lustre.—According to German patent 78,731, a preparation for producing on printed curtains, and the like, the same effect as bronze powder, may be obtained by treating powdered mica with an ammoniacal solution of casein and a dissolved metallic salt, and colouring the whole with a vegetable or aniline dye.

Process for Softening, Sizing, and Loading Textile Fibres, and for Treating Yarns and Fabrics.—In the process introduced by S. Carmichael, a bath is prepared by dissolving casein in oil. If used for yarns and woven fabrics, the casein may be dissolved in a solution of soap, and mixed with the necessary loading ingredients. For example, the product may consist of—

Casein	16 parts
Soap	8 ,,
Mineral or other oil	60 ,,
Water	300 ,,
Loading	200 ,,

The casein must be free from any acid impurities.

The materials to be treated are immersed in a bath prepared by swelling casein in an aqueous solution of glycerine, lactic acid, dye, and the necessary loading ingredients. Ten parts of powdered casein are mixed with 50 of water and a solution of 2 parts of glycerine (30° B.) in 100 of water, the necessary dye and loading ingredients being added when the casein is thoroughly swollen. This casein bath may be acidified with 2 to 4 per cent. of lactic acid, without producing any precipitation of the casein itself. By means of this bath it is possible to finish and dye fabrics in an acid liquid, which was previously impracticable with alkaline solutions of casein.

Fixing Casein and other Albuminoids on the Fibre, more particularly in Dyeing.—Vegetable fibres, *e.g.*, cotton, jute, or flax, are steeped in a solution of casein in hydrochloric acid, phosphoric acid, or lactic acid, and subsequently treated with a saline solution such as sodium sulphate, ferric acetate, sodium bichromate or sodium tungstate, capable of throwing down from the casein solution a precipitate that is insoluble in water. For instance, 10 parts of casein are dissolved in 200 of water and 1 part of 25 per cent. hydrochloric acid. The cotton is steeped in this solution, and, after the excess liquor has been removed by squeezing, it is passed through a warm 10 per cent. solution of Glauber salt, and then washed. The hydrochloric acid may be replaced by an equal amount of 25 per cent. phosphoric acid, the material being afterwards treated with ferric acetate and washed (German patent 139,565).

Fixing Insoluble Colouring Matters.—The colours to be fixed are printed with size or casein, the fabric being then steamed or treated with a solution of formaldehyde. The resulting insoluble compound of the latter substance with the size or casein, envelops the colouring matter, thus fixing it on the fibre, and rendering it waterproof. The printing colour, prepared with dissolved size or casein, is treated with the ammonia or bisulphite compound of formaldehyde and printed on the fabric. This printing colour does not coagulate at ordinary temperature; it is only when the printed fabric has been steamed or heated that the formaldehyde compound is decomposed, the liberated formaldehyde combining with the size or casein to form an insoluble compound. This method has been patented and used in Great Britain. In another system the printing colour is prepared with casein, the printed and steamed fabric being exposed to the action of formaldehyde.

Waterproofing and Softening Dressing.—The finishing of textile fabrics has hitherto consisted in impregnating them with a soluble dressing and then drying them, the dressing thereupon solidifying on the fibre making the material more or less stiff. This system, however, is attended with the defect that when the fabrics are moistened the stiffness soon disappears owing to the solubility of the dressing. The defect in question can now be obviated by impregnating the fabric with a soluble mass that is capable of conversion into an insoluble form by means of chemical or physical agents. According to a process patented in France, the fabric is treated in the cold with a mixture of casein, albumen or gelatine, and formaldehyde or hexamethylenamine, then dried at 80° C., and finally steamed. The solution of the colloidal substance may also be incorporated with pigments or loading ingredients, such as barium sulphate, these being fixed on the fibre when the albumen is hardened by the formaldehyde. Casein and gelatine are used in the form of 10 per cent. solutions, while the aqueous solution of formaldehyde is of 1 to 2 per cent. strength. Formaldehyde bisulphite is prepared by mixing 8 parts by weight of 40 per cent. formaldehyde with 10 of sodium bisulphite of 30° B. strength. The hexamethylenamine is obtained from 8 parts of formaldehyde and 10 of concentrated ammonia.

Casein for Mercerised Crêpe.—According to a German patent process, the fabric is printed with casein or albumen, steamed to produce coagulation, passed through a concentrated solution of caustic soda (30° to 35° B.), squeezed between rollers to express the superfluous lye, hung up for a time to prevent an undue rise of temperature in consequence of the mercerisation process, then acidified with dilute hydrochloric acid, washed and dried on a tentering frame.

Fixing Zinc White on Cotton with Formaldehyde.—The use of formaldehyde or formalin in cotton printing is based on its property of coagulating casein, albuminoids, glue, etc., and rendering them insoluble. Thus, in printing metallic powders and pigments on cotton fabrics, use can be made of a compound of casein or gelatine and formalin (Schering). Moreover, formalin can be employed with advantage for fixing zinc oxide, printed in a medium of casein and borax on thin, transparent fabrics or on mercerised cotton goods. The fabric remains soft, and the dull zinc white produces a pleasing effect in contrast with the glossy ground; it can also be toned to any desired shade by the addition of pigments. At the same time it appears that the action of the formaldehyde on the casein is more rapid and thorough in an atmosphere of steam than in ordinary air. The fabric is therefore put through a Mather and Platt machine, in which the formaldehyde is vaporised and the zinc white is so firmly fixed on the fibre that it will withstand boiling with soap for a quarter of an hour. Finally, it should be noted that the casein colours fixed with formaldehyde are as pure in tone as those obtained with egg albumen, whilst considerably lower in price.

W. Kay & Schoen print the cotton fabric with a colour compounded of 3½ parts of zinc white and 1½ of casein-borax medium; the goods being afterwards steamed for five to ten minutes. In the bottom of the steamer is arranged a perforated pipe, through which formaldehyde (40 per cent.) is admitted in order that it may be vaporised in the steam chamber and thus fix the casein and zinc white on the fibre.

Casein is used for waterproofing fabrics and in calico printing, being rendered insoluble by exposure to the vapours of formaldehyde (J. E. Bousfield, F. Cantin, G. Miglioretti and G. Maffei, English patent 1,160, 1901).

Casein-Magnesia.—Ten parts of powdered casein, 40 of water and ¾ part of magnesia are stirred together for twenty-four hours at the ordinary temperature, and afterwards added to a solution of 0·3 part of barium hydroxide in 30 parts of water, the whole being warmed to 95° F. for some time. An excess of barium hydroxide is injurious. This preparation will fix mineral pigments sufficiently to be fast to washing.

Casein Medium for Calico Printing.—Six parts of casein are well stirred up with 50 of water at 120° F., and left to settle. The clear liquid is poured off and the residue is mixed with 1 part of borax dissolved in 12 parts of water.

Chevalott's Waterproofing Process.—The Chevalott process is designed to deprive textile fibres of their capillarity, and thus prevent them from absorbing water, without obstructing the interstitial spaces between the threads in the fabric. The process is especially suitable for materials that are to be worn next the skin, and have to be frequently washed, *e.g.*, underlinen, clothing, etc. At the same time the fabric retains its softness and permeability to air, and can be washed with soap, benzine, etc., without affecting its waterproof properties. The preparation consists of a mixture of about 40 parts of casein and 200 of water, stirred up until of about the same consistency as cream. To this is gradually added about 1 part of lime slaked to powder, which furnishes a viscous fluid mass. At the same time 20 parts of neutral soap are dissolved in about 240 of water and mixed with the casein solution. The fabric is impregnated with this mixture, so as to about double its original weight, and is then entered in a solution of aluminium acetate at about 120° to 140° F., which renders the casein insoluble and also reacts with the alkaline soap to form an insoluble aluminium soap. Finally, after having entered the fabric in nearly boiling water, it is dried and ironed.

Loading Silk.—According to a patent granted to the Chemische Fabrik auf Aktien in Berlin, the silk is repeatedly soaked in a solution of casein or size, which may also contain an addition of metallic salts. By afterwards exposing the fabric to the action of formaldehyde, its weight may be increased in this way by 30 to 50 per cent., without metallic adjuncts. At the same time the gloss and scroop of the silk are improved and the fibre is strengthened.

Threads, Blocks, Plates, etc., of Casein.—According to H. Timpe (French patent 356,508, July 28, 1905), casein can be converted into threads (like artificial silk), blocks, plates, etc., by treatment in the following manner: When an alkaline solution of casein or paracasein is treated with acetone and boiled it separates into two portions: one soluble, the other forming a flocculent white precipitate, which will settle down by subsidence alone unless the solution is too viscous or too concentrated. It is, however, more rapidly removed by means of a centrifugal separator. The liquid portion is limpid and viscous, and when dried forms a clear mass of considerable hardness which becomes plastic on heating, and in this condition may be rolled out into thin sheets or drawn into threads.

The casein may also be dissolved by solutions of alkali sulphocarbonates, and coagulated by ammonium sulphate, the product being drawn into threads, films, etc. (French patent 395,402, 1907, and addition thereto, July 31, 1909).

Sizing Material.—H. V. Dunham, Bainbridge, New York, assignor to the Casein Company of America (U.S. patent 897,885, September 8, 1908), claims the production of a compound of hydrofluoric acid with casein—caseinate of hydrofluoric acid—formed by the addition of commercial hydrofluoric acid to heated milk, the proportions being 0·5 to 1 part of acid to 1,000 parts of milk. This product, mixed in the proportion of 94 parts with 6 parts of borax and a sufficiency of water, is recommended for sizing purposes.

For sizing purposes, T. J. Denne and A. Hentschel dissolve the casein in ammonia (English patent 2,429, 1872).

CHAPTER X.

CASEIN FOODSTUFFS.

It is a well-known fact that animal albumen is a very important ingredient in the food of man; and it may also be accepted as proved that man should take one-third of his requirements of albuminoids in the form of animal food. In this connection, meat is the principal form of nourishment possible, since eggs, milk, and milk products have not the same importance for dwellers in towns, soldiers and sailors, and others similarly situated, as they have for country people. Besides, meat is the only form of animal food that man can continue to take with pleasure in sufficient quantity to satisfy the demands of the body for albumen; in the case of milk or vegetables, the consumption of the necessary quantity sooner or later, with most people, causes a distaste for the article. Now, in order to provide meat supplies at a price which would enable the bulk of the populace to purchase a sufficiency for the purposes aforesaid, it is not enough to merely have recourse to cheap imported meat. On the one hand, there is the difficulty of excluding disease, and, on the other, the alterations to which the meat is exposed (drying, pickling, smoking, etc.) in order to make it keep, frequently affect its flavour and digestibility.

For this reason, said Dr. Adolf Jolles, in a paper read before the Industrial Association of Lower Austria, it is easy to understand that the endeavours of modern chemistry should have been directed to the discovery of some substitute for the scarce commodity, animal albumen. The results of these endeavours have been utilised industrially, with the result that there are now on the market a number of preparations complying more or less with the requirements of the times. These requirements are as follows. In the first place, the meat substitute must be relatively cheaper than animal albumen. Secondly, it must be tasteless, inodorous, of the character of flour, and not more than faintly tinged with colour. Thirdly, it must be free from micro-organisms, and be capable of keeping for any length of time without undergoing alteration; and, finally, it must be suitable to and assimilable by the organism when taken in considerable amount.

The first substance coming under consideration as a raw material for such preparations is milk, on account of it containing casein. The cereals and leguminosæ are also highly important, as cheap and readily available materials rich in proteids. The number of such preparations is extremely large, but only the chief of those made from casein will be dealt with here.

One of the cheapest preparations obtained from milk is that known as *Lactarine*, which cost originally only about 4½d. per lb. This preparation, which has been on the market since the beginning of 1898, is an extremely fine white powder, soluble in water, having the following composition: water, 9·92 per cent.; fat, 0·4 per cent.; casein, 78·16 per cent.; non-nitrogenous (carbohydrates), 7·77 per cent.; mineral matters, 3·75 per cent. With regard to the assimilation of this preparation by the human organism, there is no information at present available; nor, indeed, are there any other particulars as the method of manufacture is kept secret.

Galactogen costs about 1s. 10d. per lb. It is made from skim milk by the addition of a patent preparation. The albumen contained in the product is not coagulable by the heat of boiling water. The chief constituents are: fat, 3·5 to 4·5 per cent.; proteids, 70 per cent.; and phosphoric acid, 1·5 to 2·5 per cent. The flavour is agreeable, and the preparation is said to be very palatable. As usual with milk preparations, it is mixed with other foods.

Guttmann's Nutrient Milk Flour.—This milk food is a mixture of several ingredients. Skim milk casein is mixed with prepared carbohydrates, mainly gluten-free oatmeal and a small quantity of aromatic substances. The preparation is a fine white powder of agreeable flavour, and its proteid is soluble in water. The composition is as follows: dry matter, 92·7 per cent., of which about 20 per cent. is albuminoids, 65 per cent. carbohydrates, and 4 per cent. fat. It is said to be very digestible and liked by children and dyspeptics. Its chief characteristic is the large proportion of readily digestible carbohydrates; and for this reason its employment might be indicated in suitable cases.

Sanatogen is another casein preparation. It is made by a patented process, and consists of 95 per cent. of casein and 5 per cent. of sodium glycerophosphate. It is a whitish powder, inodorous, and nearly tasteless. Some people experience a disagreeable after-taste on first taking this preparation and do not grow accustomed to it for some little time. Sanatogen is assimilated in precisely the same way as meat albumen; and, according to the results of experiment, the assimilation is good.

Eulactol is also a mixed product. It is prepared by evaporating milk, according to a patented process, by exposure to a temperature not exceeding 98° F., *in vacuo*, since otherwise the fat would sustain alteration, leading to early rancidity. The explanation of this appears to be that the fat globules are surrounded by an albuminous envelope, which is destroyed at higher temperatures, thus exposing the contained fat to the air, whereas ordinarily it is protected therefrom by the said envelope. Eulactol contains 33·25 per cent. of proteids, 46·3 per cent. of fat, 14·3 per cent. of carbohydrates, and 4·3 per cent. of saline matter. It is a fine white powder, in which both the albuminoid constituents and the carbohydrates are mainly soluble. The preparation is said to have been consumed by individuals for long periods and in large doses and to have been well assimilated, though no definite experiments have been reported. On account of its low proportion of albuminoids the preparation cannot be classed along with others of the same type.

The method of preparing *Dr. Riegel's Milk Albumen* is described in the patent specification as follows: The curd is precipitated from milk by means of ethylsulphuric acid, instead of the acids usually employed. This treatment leaves the casein undecomposed, and throws it down in a compact, non-mucilaginous condition. At the same time it is almost entirely free from ash constituents at the first precipitation, owing to the solubility of the lime salt of ethylsulphuric acid. The content of free sulphuric acid is also very small. The precipitation is effected with a dilute solution and at a temperature of over 86° F. It has been observed that the casein contains a considerably smaller number of germs than that obtained by acetic acid or lactic acid precipitation, this being attributed to the germicide properties of ethylsulphuric acid. The preparation is free from pathogenic organisms. Analysis reveals the following composition: casein, 86·13; water, 8·23; fat, 0·31; mineral matters, 5·27. The preparation is readily soluble in water, is devoid of any specific odour, and has a by no means disagreeable flavour when taken in small quantities. No experiments in natural digestion have yet been made with the preparation.

Plasmon, formerly known as caseon, is an albuminoid preparation obtained from milk. It is a yellowish-white powder, of medium fineness, inodorous and with a faint flavour resembling sweet milk. It contains 75 to 80 per cent. of casein, 5 to 7 per cent. of sodium carbonate, and 5 to 10 per cent. of fat and milk sugar. There has been considerable discussion respecting the probable presence of bacteria; but at all events it appears to be free from tubercle bacilli. A more important point, however, in connection with plasmon is its assimilability; and on this point opinions are unanimous, all the experiments with it having given favourable results. Moreover, it has been repeatedly determined that casein is equal in nutrient value to lean meat, and is readily absorbed in the intestinal canal. Plasmon can be used in a variety of ways. For instance, it can be mixed with an equal quantity of sugar, then boiled with water and eaten in this form; and it can also be advantageously baked into bread along with flour. Plasmon solutions may be incorporated with other foods without affecting their flavour in the slightest degree; and, finally, plasmon biscuits, plasmon cocoa, and plasmon chocolate are prepared and sold.

Dr. Schreiber says of fresh casein that it may be used as a substitute for soup, and may be incorporated with flour in bread-making without having any great influence on the flavour, though greatly increasing the percentage of proteids at a very low cost. For this purpose the casein is preferably prepared by acting on skim milk with commercial rennet, the precipitate being drained from the whey and passed through a sieve or mill, which delivers the product in the form of fine flakes. These must be used while fresh, or they harden.

Nutrium is a foodstuff prepared from casein, common salt, and milk sugar. According to F. Bimbi, it forms a white or yellowish powder containing 29·1 per cent. of nitrogenous substance. It dissolves in water, forming milky flakes and giving an acid reaction.

Casein Food.—A casein food, which dissolves without any separation of gelatinous casein when boiled in water, is obtained by mixing casein or its salts with substances containing albumose or peptone.

Casein as a Substitute for Egg Albumen.—According to Pansiot, casein treated in the following manner is suitable for replacing egg albumen for industrial purposes. The casein, mixed with water, is mixed with an excess of alkali, preferably soda, and is then treated with 5 to 10 per cent. of its own weight of sodium peroxide, added by degrees, with vigorous stirring. The mixture is gradually heated to 65° to 70° C. without ceasing to stir the mass, and the oxidation of the casein may be regarded as complete when the solution becomes clear and all liberation of gas ceases. This clear solution is cooled to 15° to 20° C., whereupon small quantities of dilute hydrochloric acid (1 : 10) are stirred in till the mass becomes milky. The precipitate is allowed to subside, collected, and pressed to remove the water containing surplus saline matters, after which it is washed by trituration with water, care being taken not to prolong the operation which would lead to solution of much of the product. Finally, the precipitate is spread out on sheets of glass, and dried either in the open air or by a current of air heated to not more than 35° to 40° C., or in any other convenient manner. The product is slightly yellow, translucent, and suitable for replacing egg albumen, the properties of which substance it possesses.

Synthetic Milk.—According to W. Hall's patent (December 8, 1903) synthetic milk is prepared by stirring up an aqueous solution of about 10 parts of sodium bicarbonate with 85 parts of ordinary dry casein, the mixture being well ground and treated with 2 parts of finely powdered calcium chloride, following this treatment by incorporating with the product about 5 parts of powdered milk sugar and 5 of butter fat for each 4½ parts of casein present.

Milk Food.—According to S. Ramage (American patent

730,702), milk is made slightly alkaline and heated, treated with a coagulant, and the resulting casein exposed to a steam pressure of 100 lb. per square inch until converted into liquid amide caseose.

Emulsifiable Casein.—To obtain casein in a form which emulsifies when boiled in water, it is mixed with a quantity of an alkaline salt, insufficient to produce a soluble compound; and this mixture, after being moistened with water, is dried at a moderate temperature. The product on being boiled with water gives a homogeneous emulsion closely resembling milk. This preparation has been patented by the Aktien-Gesellschaft für Anilin-Fabrikation, Berlin.

Casein Phosphate for Baking.—To prepare casein phosphate for bread-making, Hatmaker mixes a syrup of monocalcium phosphate, $CaH_2(PO_4)_2$—free from sulphuric acid—and water with casein that has been precipitated from milk by means of an acid and freed from milk sugar, salts, and soluble impurities by washing with water. These ingredients are intimately mixed by putting them through a mill, or in any other suitable way, and the resulting thick, uniform mass is finely dried at a low temperature *in vacuo* and reduced to powder.

Another patent by the same inventor relates to the preparation of a stable, non-hygroscopic compound of casein with phosphoric acid, by concentrating an aqueous solution of phosphoric acid to a syrupy consistency along with 1 part of casein, and then intimately mixing this with the rest of the casein, drying and grinding the product. This may be mixed with an equal quantity of sodium bicarbonate and used in bread-making.

Bernstein's Baking Preparation.—A baking preparation consisting of casein and albumen is obtained by heating skim milk, precipitating the casein, and converting the same into a creamy condition by further mechanical treatment.

Making Bread, Low in Carbohydrates, from Flour and Curd.—Crude casein forms a useful adjunct in bread-making, but in the ordinary method of baking its use is merely a restricted one, since any excess over a very limited quantity injuriously affects the dough, preventing it from rising properly. At the same time the milk sugar introduced in the curd remains in the bread. These two drawbacks to the use of the bread for invalids can be obviated by adding to the dough and casein a proportion of peptone, albumose (or substances containing the same), digestive extracts, albuminoids, or derivatives thereof.

Higgins's Casein Food.—Casein is precipitated from skim milk by hydrochloric acid, the product being dried, ground to powder, and mixed with flour, rice, grits, tapioca, oatmeal, arrowroot, bran, sugar, etc.

Preparing Soluble Casein Compounds with Citrates.—Milk casein, in the moist state, is rubbed down with trisodium citrate, with or without an addition of sodium bicarbonate or trisodium phosphate, and the product is dried.

Casein Food.—Milk casein or curd is dissolved and its acidity, determined by testing, is partially neutralised, the resulting mass being dried, sterilised and used as a foodstuff.

Sell's Curd "Zwieback" Rolls.—Precipitated casein is mixed with milk sugar, exposed to the action of kephir ferments and neutralised, the product being absorbed by Zwieback powder (Zwieback is a kind of roll made in Germany) and dried.

Food Powder.—Casein is treated with a suitable digestive agent or enzyme which renders it soluble and at the same time partly peptonises it. The process is arrested by drying the product in thin films on cylinders heated to a temperature of about 212° F., whereby it forms a product which is easily pulverised, forming a very nutritious food (A. A. Dunham, New York, assignor to the Casein Company of America, U.S. patent 750,832, February 2, 1904).

Substitute for Egg Albumen.—A rather remarkable product is the subject of a patent granted to A. Berstein (French patent 347,135, October 15, 1904). This material is formed by dissolving 100 parts of casein with 650 parts of water, and 35 parts of ammonia solution (sp. gr. 0·98). To this is added 35 to 45 parts of sodium silicate and sufficient acetic or hydrochloric acid to render it nearly neutral. The result is a thin fluid, but on heating it becomes much thicker and is then suitable to be used for cementing purposes. On evaporation at a low temperature it yields a dry product which it is stated can be used in place of egg albumen.

CHAPTER XI.

SUNDRY APPLICATIONS OF CASEIN.

Uses of Casein in the Paper Industry.—An important part is played by adhesives in the industries wherein paper is employed, both in order to inseparably fasten together individual sheets of paper, convert paper pulp into a mouldable condition, and also for the application of thin layers of colouring matter or other coatings on paper or millboard articles. Such coatings may be either matt or more or less glossy, but in any event must be able to withstand to a certain extent the influence of moisture. For all these purposes casein is, *per se*, admirably adapted, since it will cement sheets or bands of paper together and forms thin coatings of considerable elasticity either alone or in association with other substances, colouring matters in particular. When a solution of casein is treated with small quantities of formaldehyde, and the article coated with the preparation is exposed to the air, a number of new products can be obtained. Thus, for instance (by patented processes) we obtain waterproof paper that can be used instead of guttapercha paper, waterproof cardboard boxes and cartridge cases, washable wall papers, washable paper garments, coloured papers, art papers, transfer papers, and so on. Utensils, more particularly basins, dishes, and the like, made of paper pulp or millboard, can be rendered waterproof by treatment with formaldehyde, and used for a variety of purposes, *e.g.*, as developing dishes in photography. Similarly, cardboard treated in the same way can be used for stereotype matrices, which will keep for any length of time, by reason of its lightness and durability. It is thus evident that the field of application open to casein is practically illimitable.

Metachromotype Paper.—This paper, which is used for transfer pictures, is preferably made of a fairly good, unsized or lightly sized but smooth paper, capable of readily absorbing the thin solution of casein (preferably prepared with sodium bicarbonate) and of softening with similar ease when it has to be released. Since imperfectly coating the paper with the adhesive will result in a defective impression, it is evident that the coating must be perfectly uniform. The operation is best performed with a flat brush, the paper being spread on a table and the casein solution applied smoothly by working the brush in one direction. If necessary the coating is repeated, the brush being then worked at right angles to the previous direction.

The prepared paper is next hung up to dry on lines in a gently warmed room, preferably in a stretched condition to prevent it curling. It is afterwards cut into sheets and packed, either with or without calendering to smooth the surface.

Sizing Paper with Casein.—Notwithstanding the most scrupulous care bestowed on the preparation of the resin soap used in sizing paper, it has been found impossible to impart the desired firmness and impermeability to the paper by the use of vegetable size. In view of the large quantities of casein now obtainable as a result of butter-making on the large scale, in which casein has had only a very limited application, it seemed advisable to test its suitability for sizing paper; and with this object comparative experiments were carried out by Dr. Zanardi with resin soap and casein solution.

Paper pulp was mixed with dissolved casein for twenty minutes, and to the mixture was added a solution of alum

—as in resin sizing—followed by diluted sulphuric acid until a faintly acid reaction was produced. In the trials the casein was poured on at the same time as the resin soap, or else after the latter had been precipitated by aluminium sulphate. In general the addition of casein was found to have a favourable influence on the firmness of the paper and on the amount of size consumed. Casein can also be used for this purpose by itself, furnishing a coating that will make the paper easier to roll up.

Waterproofing Paper.—This process is devised for making paper and fabrics waterproof to such an extent that they will stand protracted exposure to the influence of moisture without losing their softness and elasticity. At the same time they are made superior to paper or fabric coated with caoutchouc, both from the point of durability and freedom from smell.

The principal features of the process are that the paper or other material to be waterproofed receives two waterproof coatings in succession, the first consisting of a specially prepared solution of glue or casein (or mixture of both), which, when warmed and treated with certain additions, remains permanently supple and elastic.

In carrying out the process, glue or casein is dissolved in water or other suitable solvent and treated with an addition of sodium tungstate to improve the tenacity (if desired), the albuminous substances being then precipitated by tannin or other suitable precipitant as a viscid insoluble mass.

This mass, which is elastic and plastic while moist, becomes very hard and brittle on drying, so that it would be entirely unsuitable for the purpose in view were it not corrected by melting it in a pan (preferably before it has set) and adding glycerine, syrup, molasses, fats or oils, alone or in conjunction, the whole being well mixed. The quantity of materials so added depends on the degree of suppleness desired, and is preferably about one-half of the mass obtained by the aforesaid precipitation.

The resulting mass for the first coating can be applied to paper or fabric before it has set, forming a very flexible, insoluble coating resembling caoutchouc. To make the paper keep better it may be at once mounted on fabric by pressure, or pressed between two similarly treated sheets or roll lengths of paper. Of course the fabric may have been impregnated beforehand, or else the joined paper and fabric may be treated afterwards.

To improve the waterproofing qualities and impart a fine gloss, a second coating is applied consisting of any convenient waterproof varnish or lacquer. Colouring matters can be incorporated with the first or second coating, according to choice.

Casein Solution for Coating Paper.—A casein solution, suitable for coating paper and for other purposes, can be prepared, according to W. A. Hall's English patent, by mixing casein (precipitated with hydrochloric acid) with 10 to 15 per cent. of its weight of sodium phosphate, preferably trisodium phosphate, and 1 to 3 parts of water to each 1 part of casein.

Horn's Clear Solution of Casein.—A clear solution of casein, free from fatty substances, is obtained by treating a 10 to 20 per cent. solution of casein with 7 to 8 per cent. of caustic potash (according to the amount of dry matter), the whole being shaken up with ether for a short time and run into a settling vat. The clear solution of casein subsides and can be drawn off.

Facing for Paper.[1]—Casein 1 lb., water 3½ lb., borax 3 oz., these are heated together until dissolved. Ammonia may

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[1] On the testing of casein for paper facing, see E. Sutermeister, "Paper Making," 1914, **33**, 140-143, 187-190. This author states that casein precipitated by rennet is not suitable for use in paper-making.

be used in place of borax in the proportion of about 1 part of strong ammonia to 5 parts of casein, with water sufficient to form a workable fluid. The white materials used for facing consist of China clay and satin white in the proportion of 75 parts of clay to 25 parts of satin white.

For glazed or faced waterproof papers, of good quality and in any colour, 100 parts of pure casein are mixed with 1,150 parts of cold water, 15 parts of borax being then added, and the mixture thoroughly stirred. Heat is applied by means of steam until a temperature of 70° C. is reached which must not be exceeded. When the solution has become perfectly homogeneous it is strained through a sieve, and there is added thereto 750 parts of kaolin, satin white, or other white material, followed by 10 parts of 40 per cent. formaldehyde, and, when specially pure whites are desired, a little ultramarine also. A cheaper formula for low grade papers consists of: 100 parts of casein mixed with 1,150 parts of water and dissolved in 30 parts of ammonia 26° Bé. (or 50 parts of soda solution 6° Bé.).

For a sizing material for paper 100 parts of casein are mixed with 450 parts of water and 15 parts of sodium carbonate, the whole being stirred till thoroughly mixed and heated at a temperature below the boiling-point until completely dissolved. The size may be obtained in a thicker condition by reducing the quantity of water. This solution increases the beauty of colours, facilitates the finishing operations, and imparts properties which are useful in the printing and folding, besides imparting a silky feel. Paper sized in casein solution can be damped by immersion in hot or cold water, and will receive and retain the ink after drying, just as though it had not been damped. This property is especially valuable in connection with State papers, and other important documents which it is desirable should be protected from damp.

Water- and Fireproof Asbestos Paper and Board.—An essential preliminary to the manufacture of asbestos board is to isolate the asbestos by chemical means, in order that it may retain its flexibility in presence of the subsequently added ingredients, and not become brittle. This treatment is preferably effected by means of an acid, a saline solution, or dilute glycerine, the latter being more convenient in practice. The asbestos is first mixed with 4 to 6 per cent. by weight of glycerine, followed by 5 to 10 per cent. of water. The medium formerly used for binding together the fibres of asbestos was fish glue (especially in the Ladewig process); but casein will accomplish the same purpose more effectually and at far less cost.

The mixed asbestos and casein (*e.g.*, casein and borax solution) is next reduced to a fine pulp in a mill. This impregnation isolates the asbestos fibres and prepares them chemically in such a manner that they are no longer exposed to any injurious action on the part of subsequent adjuncts, as was formerly the case.

The well-ground mass is treated with 2 to 3 parts of rosin soap (previously dissolved in hot water), the whole being well mixed and afterwards treated with about 6 parts of zinc chloride dissolved in 15 to 25 parts of water, and finally 20 parts of graphite in suspension in about 50 parts of water is added. The graphite makes the mass fireproof and imparts to it the appearance of vulcanite.

For use as a packing material in pipe joints that have to be frequently opened, this material may be covered with wire gauze on one or both sides.

The finished, intimately mixed mass is worked up into paper or millboard of any desired thickness, in the machines usually employed for these purposes. The product is afterwards pressed, dried in the air, and impregnated with a 1 per cent. solution of zinc chloride. It is then redried, passed through a ½ to 1 per cent. aqueous solution of rosin soap (prepared by dissolving the rosin soap in spirit and diluting with water), and finally dried again in the air. The appearance is improved by calendering. The finished article is elastic and completely fire- and waterproof.

Asbestos millboard is prepared as follows:—

Whereas long staple asbestos is required for spinning purposes, the short fibres of ordinary quality are more suitable for the purpose now in view. The short fibres separated from those of longer staple by screening, prior to the spinning process, are also used. The crude asbestos is put through an opener to break up the fibres, and the material is then softened with boiling water, after which it is ground in a mill of exactly similar type to those employed in paper-making. This consists of a long, rectangular, wooden, stone or iron trough, filled with water and containing a revolving roller provided with steel rails, underneath which is arranged a massive oaken block inlaid with a row of knives. The trough is divided into two parts by a central partition, over which the asbestos fibres are flushed by the water into the working compartment, where they are acted on by the roller and knives. A hood placed above the roller prevents any of the fibres being thrown out of the trough by centrifugal force. Means are provided for setting the roller progressively closer to the knives, so as to reduce the fibres more and more. At the same time the medium—casein, starch, gum, etc.—employed to bind the asbestos together, is usually added in the mill.

The further treatment of the asbestos pulp is on precisely the same lines as in dealing with paper pulp for the manufacture of machine-made paper. The pulp is delivered on to an endless seive of metallic gauze, to which is imparted a vibratory motion to facilitate the draining away of the water; after which it is passed between rollers to squeeze out more of the water. By means of an endless belt the pulp is next fed to a second pair of rollers, after leaving which it still contains a considerable amount of water. It is cut up into squares, which are placed between zinc plates; a number of these alternating layers being put into a powerful hydraulic press, after leaving which the pulp boards are hung up in a steam-heated chamber, to get rid of the last traces of moisture.

Asbestos boards can, of course, be made in varying thicknesses. The ordinary makes are composed of 6 to 12 and even more layers, placed one above another and united by passing them between rollers and in the hydraulic press. The usual thicknesses are ½, ¾, 1, 1½, 2, 2½, 3, 4, 5 to 10 and 15 millimetres, the sheets being generally 40 inches in length and breadth.

The chemical composition of the mass varies to an extraordinary degree. Most kinds are greatly adulterated, containing not more than 50 per cent. of asbestos, and that, too, of inferior quality. It cannot be too strongly emphasised that the valuable properties of the asbestos are the more apparent in proportion to the quality of material used and adjuncts are shunned.

Paper Flasks, etc., for Oils and Fats.—Vessels of different shapes can be manufactured from paper by reducing well-sized paper to pulp. A useful paper for this purpose consists of about the following proportions:—

Rag	10 parts.
Straw	40 ,,
Brown cellulose	50 ,,

The paper is impregnated with a solution of casein, in order to render it impermeable and at the same time to make the individual sheets of paper adhere together. With this object in view the sheets of paper are coated on both sides with an ammoniacal solution of casein, laid one on top of the other, and at once placed in heated moulds, the pulp being forced, by means of a press, into a tray or basin of the form most suitable for the purpose in view.

The moulds are made in two halves, one hollowed, the other raised, and fitting into it, leaving sufficient space for the pulp. In the case of a flask or bottle, for instance, the hollowed portion is fitted at the top with a lug for receiving the stopper, with the neck, and, underneath, the part on which the bottle is to stand. The stamping mould is gently warmed before the paper is inserted, so that the casein solution sinks more deeply into the fibres of the latter, and at the same time the ammonia has a better chance of evaporating. After a short time the paper mass will have set hard, when the finished half bottle can be taken out, and left in the air to dry completely. These halves are afterwards thinned down at the edges where they are to be joined, pressed together, cemented with casein glue, and coated with a thin layer of casein solution both on the interior and exterior.

Washable Drawing and Writing Paper.—Any convenient kind of paper is treated with a first coating of casein, size, or other suitable medium containing an admixture of some finely pulverised mineral substance, such as zinc white, chalk, lime, heavy spar, etc., and the requisite colouring matter. It is then brushed over with, or dipped in, water-glass containing a small quantity of magnesia, and left in the air for a short time to dry, at a temperature of about 77° F. This second coating may be replaced by one of dilute formaldehyde.

Paper treated in this way may be written or sketched upon with pencil, chalk, coloured crayon, charcoal, transfer ink, or lithographic ink; and the marks thus produced may be washed off again without any appreciable alteration of the paper.

Paper of this kind possesses the advantage of economy when used in schools or by designers. In drawing plans, for instance, the design can be easily and rapidly removed with a damp sponge, and a fresh drawing made at once on the same sheet. Such paper forms an excellent substitute for the heavy slates used in schools for writing and drawing lessons; and is advantageous for this purpose, inasmuch as it can be made in colours that will not fatigue the eye.

Nevertheless, it cannot be denied that repeated writing and washing soon wears out the protective coating, so that the sheets do not last very long, especially under the heavy wear to which they are subjected in school work.

Paper Wrappering for Food, Clothing, etc.—The customary practice of protecting clothes from the ravages of moths and other insects by bestrewing the articles with naphthalene, camphor, pepper, and so forth when they are laid away for some time, is attended with numerous inconveniences, not least of which is the unpleasant smell of the substances in question. These can be avoided by the use of paper or linen prepared by a simple process in such a manner as to permanently resist insect attacks, and also atmospheric influences, so that they may be used in packing goods destined for consignment to a distance.

The process itself is based primarily on the well-known disinfectant properties of formaldehyde, and on its capacity for forming a waterproof coating with the aid of casein.

Hence, if paper and similar materials or finished articles made from the same, such as bags, wrappering, and the like, be soaked in a warmed solution of casein, containing an admixture of wax, soap, caoutchouc solution, etc., for imparting increased flexibility, and these impregnated articles be then dipped in a solution of formaldehyde, they will become covered with a thin insoluble film. While this is still moist, several sheets of the prepared paper, or of such paper and linen, can be united together to form a more or less thick and compact material. Finished cardboard goods, boxes, etc., can also be covered by the same means with such moth-resisting paper. It is also advantageous to fasten cotton wool on to paper or linen by means of the formalin-casein adhesive or by sewing, and then impregnate the wadding with formaldehyde.

If, on the other hand, greater importance is attached to the waterproof character of the preparation, this result may be attained in various ways, for instance, by steeping the paper in a solution of paraffin in benzol, a solution of shellac and borax, alcoholic solutions of rosin, or by coating with viscose (cellulose thiocarbonate), either in conjunction with dissolved casein or following the treatment with the latter. Fine fabrics may be waterproofed by the same means or in conjunction with alumina, aluminium mordants, ammoniacal copper oxide, oil, etc.; in any case, however, a liberal amount of formaldehyde must be used. If the effect is found to have weakened by lapse of time, it can be renewed by the application of formalin (40 per cent. formaldehyde).

Materials rendered in this manner proof against germs, water and insects, are manifestly applicable to a large number of purposes. Among these may be mentioned the storing and conveyance of foodstuffs, especially in humid climates; also as wrappers for anatomical and zoological preparations, and other objects liable to decomposition. Furthermore, they may replace the more expensive oiled linen wherever a light, but resistant, waterproof and cheap wrappering is needed. Special attention is called to the manufacture of impregnated paper bags, which would meet with a ready sale for storing clothes; also portfolios for storing documents and antiquities, such as lace, water-colours, etc., in museums and collections.

Paint Remover.—During recent years the practice of removing paint by burning has fallen into desuetude. The caustic alkali preparations, however, now sold for this purpose are attended with numerous drawbacks, the ordinary substances of this class in order to be effective having to be applied several times, owing to their tendency to run down from the smooth surface of the paint, so that their action is minimised. This tendency, however, may be prevented by mixing the alkali with a very thin solution of casein, in the proportion, say, of 5 parts of caustic soda, 10 of water, and 1 of casein solution. The caustic soda is first dissolved in the water, and the casein solution is added until the preparation is of workable consistency. For use, the mass is stirred up well, laid on with a brush, and washed off, along with the remains of the paint, in about one to two hours' time. To enable this preparation to keep for some considerable time, the addition may be made of ½ per cent. of carbolic acid and a few drops of some ethereal oil, such as oil of cloves, rosemary, etc.

Beuse's Shoe Polish.—Shoe polish may be made to give a greatly improved gloss by the addition of a solution of casein, prepared by boiling in water with borax or soda. At the same time the addition of iron rosinate imparts the property of staining the leather a deep black, instead of merely forming a black coating.

The iron rosinate is prepared by adding an aqueous solution of green vitriol (ferrous sulphate) to a rosin soap obtained by boiling rosin with soda. The other ingredients of the polish are as usual: ivory black, syrup or dextrose, fat or oil. A blue-black sheen may be imparted to fine polish by the addition of a little Paris blue dissolved in water.

The following is a typical recipe for such a polish:—

Casein	16 parts by weight.
Soda crystals	6 parts dissolved in
Water	48 parts, and mixed with
Ivory Black	145 ,,
Dextrose	75 ,,
Olive Oil	12½ ,,
Iron rosinate	5 ,,

This should be further mixed with 5 parts of ferric ferrocyanide, dissolved in 1 to 2 parts of oxalic acid and 5 of water, the whole being stirred in a suitable stirrer. For solid polishes, the proportion of solid ingredients is increased.

Casein Shoe Cream.—Casein exhibits the property of furnishing with thick turpentine a handsome, shining compound, suitable for various purposes, especially shoe polish. For this purpose 4 parts of galipot are melted, strained through a sieve, and boiled with 3 parts of water and 2 of caustic soda lye (density, 37° B.) until a film has formed on the surface, whereupon another 1 part of the soda lye and 50 to 60 parts of warm water are added; 15 parts of soda crystals are dissolved in the liquid, and 10 parts of powdered casein are stirred in until dissolved. This is followed by 10 parts of grey carnauba wax, following which the whole is boiled until homogeneous. If a cooled sample be found too stiff, a little water is added. An aniline dye that is fast to alkali may be used for colouring.

Casein Photographic Plates.—With the invention of the silver bromide dry plate, which rendered outdoor photography possible, arose the necessity for replacing the support (the glass plate) by some material which, whilst possessing the transparency of glass, is free from the objectionable properties of fragility, weight and bulk.

Endeavours have been made to overcome this difficulty in various ways, but though films of celluloid, paper, mica, and gelatine have been proposed in place of glass, celluloid alone has been able to hold its own for this purpose. Nevertheless, this substance also has its defects, being in the first place highly inflammable, subject to electrical discharges which spoil the photographic image, liable to curl in the various baths, and, finally, very expensive in comparison with glass plates.

The use of casein for the purpose in question appears to have solved the difficulty of finding a material that is free from the above-mentioned inconveniences.

Wood-Cement Roofing Pulp.—This new roofing pulp has the advantage over tarred pulp in being fireproof as well as waterproof, and of not softening with heat. It is made of cellulose pulp board, painted over with the following composition:—

Slaked lime	100 parts
Casein	10 ,,

the latter being dissolved in water, stirred up to a pulp with the lime, and gradually thinned to the consistency of syrup. Four applications are generally sufficient to produce a coating of the requisite thickness.

The sheets may alternatively be dipped in the composition, the latter being in that case made correspondingly more fluid. The waterproof character is increased, and a fine gloss imparted, by applying to the finished article a coating of shellac and borax solution.

Cask Glaze of Casein and Formaldehyde.—The wooden casks used for the transport and storage of wine, beer, etc., are liable to become infested with mould fungi and bacteria when lying empty, and must therefore be carefully cleansed, before being again used, with boiling water and some disinfectant, such as lime, etc., and then dried. Even after this treatment, no security exists against the contamination of the liquid contents, or at least against their acquiring a flavour from the cask. In the case of beer barrels, it has long been the practice (in some parts of the Continent) to line them with pitch, which, however, is liable to crack and peel off, so that not only is the beer contaminated with fragments of pitch, but the cracks in the coating afford an excellent harbouring place for the development of bacteria. It is true that shellac dissolved in spirit has also been used for varnishing the interior of these casks; but that process in turn has drawbacks which preclude its employment in many cases.

It is an essential condition of a good cask lining that the coating shall adhere strongly to the wood, and that it should be insoluble in any of the liquids which may be stored in it. It must not impart to them any taste or smell, and, finally, must form a smooth coating resembling glaze, without any tendency to crack or peel off.

Such a preparation has been made by the Union Aktiengesellschaft für Chemische Industrie, of Vienna, in the form of a solution of casein and formaldehyde, which is claimed to be an efficient substitute for pitching, paraffining or varnishing beer and wine casks.

According to this patented process, the casks are lined with a small quantity of an ammoniacal solution of casein, glue, or gelatine, containing a little formaldehyde, this mixture being shaken up in the cask for a short time and the excess then allowed to drain away. The casks are next dried by the admission of heated air, and are finally rinsed out with formaldehyde solution, in order to render the film of casein perfectly insoluble.

Exhaustive experiments have demonstrated that the beer will keep in as sound a condition in the casks so treated as in those lined with pitch.

The absolutely permanent casein coating prevents any loss of carbonic acid; the coating will not peel off from the cask staves; and when it has suffered any injury from mechanical abrasion, it may be easily repaired by further treatment with casein solution. Being completely insoluble, there is no risk of the beer acquiring any flavour due to the absorption of casein.

The solution of casein and formaldehyde acts as an antiseptic; and the same property being possessed by the resulting coating, helps to preserve both the contents and the material of the cask.

The casein coating is insoluble, not only in alcoholic liquids, such as wine, beer, etc., but also in acids and weak alkalies. Hence it can also be used for casks destined for the transport or storage of liquids belonging to these last-named classes.

The Preparation of Artists' Canvas.—Large quantities of canvas are used by artists and scene painters. The material is mostly rough linen, more rarely jute, which requires—before being used for painting—to be coated with some composition that will convert the rough surface into a smooth and continuous one that is adapted to receive the paint. This operation is termed "priming," the material thus treated being known as primed canvas.

The canvas is required to be perfectly smooth and to remain so without alteration. Canvas that would warp and get out of line would distort the painting, thus causing the latter to lose entirely its artistic value. Since artists' canvas is almost invariably sold in condition ready for being stretched on a frame and painted upon, it is advisable for the maker of this prepared canvas to commence operations by stretching in such a manner that the tension will be the same in all directions. The priming composition is then applied to the surface by simply painting it on with a wide brush.

Some makers use for this purpose a composition consisting of chalk and driers, coloured grey by the addition of a dark pigment. The use of driers, however, cannot be recommended; indeed, it is probably owing to their employment that so many paintings are found to crack within a few years' time.

When the canvas is primed with a quick-drying varnish the prepared surface appears to be perfectly dry and suitable for painting on at the end of a few days, since good driers cause the material to set hard very quickly on exposure to the air. This hardness, however, is merely superficial, the under layers of the composition remaining soft for a very long time, becoming resinified only very slowly. When this resinification has reached a certain stage the stratum of varnish contracts strongly and invariably cracks.

The pigments of the painting, which are firmly attached to the priming, are constrained to follow this contraction; and this phenomenon is first manifested by the disappearance of the gloss on the surface. Examination of such a picture with a strong magnifying-glass reveals the presence of innumerable fine cracks over the whole surface; the end of the picture can then be predicted with certainty, namely, that it will eventually crack to such an extent as to become quite indistinct and worthless as a work of art.

There is, moreover, another very potent reason against the use of varnishes in preparing artists' canvas, namely, that many varnishes are made by the aid of lead preparations. It has already been remarked on several occasions that lead preparations are particularly susceptible to the action of sulphuretted hydrogen, which turns them black; and consequently paintings on such canvases will become darker coloured in course of time.

Many artists' colours in general use, such as cadmium yellow (Jaune brilliant) and vermilion, are, moreover, compounds containing sulphur. When such sulphur compounds come into contact with a priming containing lead, it follows that they will undergo an entire change, often in a few years turning brown and even quite black. Hence, even when an artist carefully avoids the use of lead pigments, in order to increase the life of his work, his precautions are rendered nugatory should he unhappily use canvas that has been primed with a composition or varnish containing lead.

For this reason the use of casein for priming offers a series of noteworthy advantages; and it is especially indicated where the risk of cracking comes into consideration. A canvas prepared with casein is more durable and comparatively cheaper than one primed with linseed oil varnish, and very little dearer than when distemper is used in priming.

Casein soluble in alkali or in water may be used, the latter being preferable since it is prepared on a manufacturing scale. The casein powder is dissolved in the following manner:—

Thirty parts of clean soft water are heated in a pan to about 176° F. and then poured into the kneading and mixing machine shown in Fig. 17, which is fitted with an arrangement for heating the trough. The stirrers having been set in motion, 5 parts of casein powder are run in by degrees, and in this way a uniform solution is obtained. It will not do to add too much powder at one time or to put the casein into the trough before the water, or a lumpy mass will be obtained instead of a thin homogeneous solution. The warming of the trough throughout the operation will prevent the solution thickening too soon.

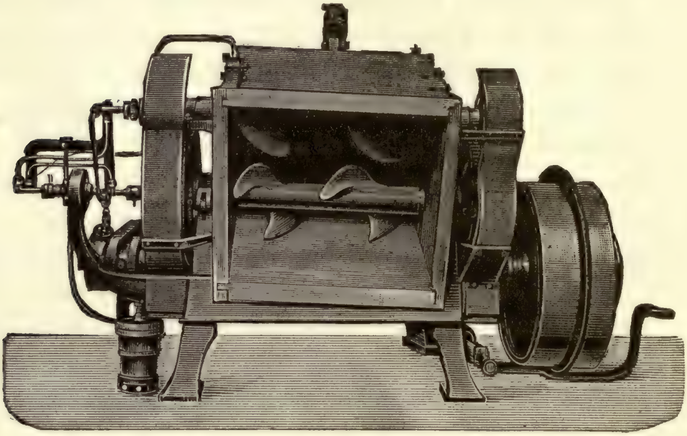

FIG. 17.—Werner & Pfleiderer's Kneader and Mixer with Heated Trough.

This solution is next applied evenly to the surface of the stretched canvas. When the coating is dry the next step is to apply the priming composition—a mixture of neutral wool fat, dissolved casein and the finest levigated chalk or lithopone. Drying oils and dryers may also be added in moderate amount if desired.

The neutral wool fat, which exudes from the glands in the skin of the sheep, and constitutes the grease permeating the wool, is met with in a purified state in commerce, as lanolin. It differs from vegetable and animal fats inasmuch as the contained fatty acids are not combined with glycerine, but with cholesterin and the so-called fatty alcohols. As a result of this constitution the fat is less affected by the influence of warmth, air, and light than the other fats of animal or vegetable origin. It remains perfectly sweet even after prolonged exposure to atmospheric influences, and unlike the true fats it shows no increase of acidity and no rancidity with increasing age. Another consequence of the peculiar composition of neutral wool fat is its high resistance to the action of alkalies and caustic alkaline earths, so that, under ordinary conditions, it is unsaponifiable. The neutral wool fats are miscible with water, and are able to absorb and permanently retain up to as much as twice their own weight of water—a valuable property when the incorporation of large quantities of water into a fatty mixture is desired. As a rule the neutral wool fats are among the most stable fats known, and their valuable qualities ensure them a progressively extending industrial future.

The elasticity and resisting properties of the mixture of casein and neutral wool fat render this composition specially adapted for grounding artists' canvas.

Another composition, suitable for photographers' backgrounds, is obtained by mixing cement or diatomaceous earth with casein solution. In this case also the durability of the priming can be increased by spraying it with a dilute solution of formaldehyde.

In the case of canvas for other decorative purposes, the power of resisting the action of the weather is a prominent necessity. The priming for this purpose may be prepared by stirring 18 parts of chalk and 2½ of earthy pigment to a pulp with water. Ten to 14 parts of casein previously treated with alkali are next stirred in, and the whole is diluted with another 10 parts of water.

For priming canvas for outside exposure, the following method is recommended: 10 parts of finely powdered casein soluble in water are intimately mixed with 10 parts of slaked lime and 90 of levigated chalk, and diluted with water to workable consistency.

Solidifying Mineral Oil.—Casein and formaldehyde are especially useful in the solidification of petroleum and other mineral oils. The oil is treated with dissolved casein or an alkali compound of the same. According to Helbing & Passmore's Patent Specification, the resulting compound is hardened with formaldehyde, and is then insoluble in water; it does not melt on heating, but the petroleum can be recovered by distillation. The product is similar in colour to the petroleum used, but is less transparent.

Uses of Casein in Photography.—In connection with the employment of casein as a medium for photographic purposes, Dr. Otto Buss expresses himself in the following terms:—

When we consider the integral character of the medium as a factor of sensitised strata in photography generally, and especially in silver chloride printing-out papers, and the part it plays in the presence of silver salts of organic acids, as well as the extent to which it influences the print and the character of the photographic picture, we cannot regard as useless any endeavour to attain perfection by the use of fresh substances as media. Just as it would be erroneous to rest content with what has been already attained in this direction, and to regard it as settled beyond question that the known media—albumen, gelatine, collodion, vegetable albumen, algin jellies, rosin, starch, etc.—fulfil all requirements, and afford sufficient means for the manifestation of the individuality of the photographer in the production of artistic effects, so also is the prospect certain that the means of artistic expression and technical advantages in photography can be widened by the adoption of new substances as media.

Among the numerous colloidal amorphous substances whose chemical and physical properties indicate the probability of their application as photographic media, a place almost in the front rank must be given to casein, which has already formed the subject of investigation for this purpose by various photographic chemists. Their experiments have remained unsuccessful, owing to the difficulty of overcoming the technical imperfections of casein strata for photographic purposes to an extent that could make their advantages apparent.

So far as these experiments have been made public and brought to the writer's knowledge, they were all undertaken with the object, *mutatis mutandis*, of dissolving casein in alkalies and employing this solution, together with the requisite quantity of chlorides to ultimately form silver chloride, to coat paper for sensitising with silver nitrate. These attempts, therefore, were directly allied to the albumen process, under the erroneous idea that casein being an albuminoid substance, would behave similarly to egg albumen.

The writer has repeated and checked a number of these experiments, and found it impossible to obtain papers of practical utility by the method in question. Pure casein was dissolved in alkalies, with the aid of warmth, both caustic alkalies (potash, soda, and ammonia) and carbonates (sodium carbonate and bicarbonate) being used, the casein being stirred up with water and brought into solution by adding the dissolved alkalies. In some cases the resulting solutions were treated with common salt or ammonium chloride and filtered, so that uniform glossy layers could be obtained on papers, either plain or surfaced with baryta. Flexibility was readily obtainable by the addition of glycerine to the casein solution. The dried papers were then sensitised in the usual way, both in neutral silver baths and in those containing citric acid. Nevertheless, although the conditions were varied in numerous ways, and the papers resembled albumen papers in many respects, the film softened, either occasionally in the toning bath or invariably in fixing or washing, and in some cases came off altogether, though this could be prevented by using an alum bath before fixing. Somewhat better results were obtained by using casein solutions hardened with formaldehyde, inasmuch as the papers then could be toned, fixed, and washed. The papers had the same general character as albumen paper, without any advantages over the latter. When sensitised, even in an acid bath, their keeping properties were very poor, which, indeed, is not surprising in view of the presence of the formaldehyde, which is a reducing agent. Further attempts in the same direction were abandoned as hopeless ; and those made with a view to using casein in the preparation of emulsions proved equally unsuccessful, a compound containing silver and casein being invariably separated in large flakes, impossible to divide sufficiently fine by mechanical means. These experiments were also abandoned ; and although it is not asserted that the use of alkaline solutions of casein in one or other of these directions is an impossibility, it would seem that some technical device of a very different character to the usual methods of working will have to be adopted to ensure success ; in any case, the writer does not at present think it likely that a normal practical method will be discovered.

An explanation of the peculiar behaviour recorded above is afforded by the chemical conduct of casein. The substance may be regarded as having both basic and acid properties, since it is insoluble in water, alcohol, ether, acetone and other known solvents, whilst it furnishes compounds with both metals and acids. The alkali compounds are readily soluble in water, whilst the compounds with the heavy metals, such as iron, copper, silver, etc., are precipitated as insoluble, amorphous, flocculent precipitates from the solutions of the alkali salts, on addition of soluble salts of the metals.

The basicity of casein is revealed by the fact that it dissolves to form an acid solution when stirred up with water and carefully treated with a dissolved alkali, whilst, after neutrality is reached, a further quantity of alkali can be added before the same appears in excess, that is to say, before the appearance of an alkaline reaction can be detected.

The alkali compound will therefore act as a dibasic salt in presence of silver nitrate, normally with the formation of a silver compound (presumably containing two atoms of silver) and alkali nitrate; and this will invariably occur, no matter in what manner the casein and alkali are brought into solution. Silver caseate, however, is by far inferior in stability to silver albuminate, inasmuch as the silver caseate image is soluble in hypo.

On the other hand, casein dissolves in dilute acids, from which solution it can be reprecipitated by neutralisation with alkali, without decomposition. The same precipitate is obtained by the use of a large number of metallic salts, such as alkali chlorides, alkali sulphates, alkali nitrates, a number of salts of the heavy metals, etc.; and this peculiarity seemed to the writer to offer a prospect of success in using casein as a medium for photographic films.

The success foreshadowed was eventually realised in the following manner: When casein is stirred up with water and dissolved in a weak solution of acid, *e.g.*, citric acid, by gentle heat, it forms a clear, gelatinous mass, which sets to a jelly on cooling. Physically, it behaves exactly like gelatine, and there is not the least difficulty in coating paper uniformly with the warmed solution. The coating sets immediately, forming a glossy stratum, which, however, is still slightly soluble in water. To render it insoluble in water and weak acids, it is treated by floating or immersing the paper in a solution of common salt or ammonium chloride, etc., and this treatment does not deprive the stratum of its permeability to aqueous solutions. At the same time, the use of a chloride in this operation imparts to the stratum the chloride necessary for the subsequent formation of silver chloride, without eliminating the citric acid. It is easy, by suitably modifying the concentration of the chloride solution, to incorporate any desired quantity of chloride in the stratum; and since, as already mentioned, the original quantity of citric acid is left unaffected, or only washed out to a very slight extent by the chloride solution, it is possible in this way to adjust the relative proportions of chloride and citric acid to any desired extent. The paper prepared in this way will, of course, keep for any length of time when dry. Sensitising is effected in the same way as for albuminised paper, in a neutral or faintly acid silver bath; but the processes involved in the operation are evidently of a very different character to those occurring in the case of albuminised paper, or such as that prepared with an alkaline solution of casein. It does not seem probable that insoluble, free casein and silver nitrate react with formation of silver caseate and nitric acid; besides which both the behaviour of the finished paper and the results of wet tests are against the occurrence of this reaction. The reaction is more probably confined to the silver nitrate, the chloride and the citric acid alone, silver chloride and citrate being formed in the casein stratum, which itself remains chemically unaltered. The behaviour of the stratum in every respect favours this assumption, which is very difficult to prove chemically, both the casein and silver caseate being insoluble; for whilst the stratum obtained by means of casein, alkali and silver nitrate is soluble when the print comes to be fixed in hypo, etc., that obtained in the manner just described remains perfectly intact and tough. The typical purple-brown colour of silver caseate could not be detected anywhere, the print having the same bluish or reddish-purple tone as the gelatino-chloride or collodio-chloride papers. At the same time, the character of the prints more nearly resembled that of gelatine papers than albuminised papers. Alkali caseates and the water-soluble egg albumen of albuminised paper, on the other hand, react on silver nitrate to form silver albuminate and silver caseate respectively. (An analogous reaction may be mentioned in the behaviour of citric acid and silver nitrate, inasmuch as alkali citrate and silver nitrate furnish silver citrate in almost quantitative amount, whereas none is formed in the case of the free citric acid and silver nitrate.)

In this manner the utilisation of casein as a medium for photographic films may be claimed to have been accomplished, inasmuch as a stratum of free casein is obtained which encloses the image-forming substances, silver chloride and silver citrate. The use of this method should certainly not be restricted to the preparation of chloride printing-out papers, but will probably find application in numerous other directions.

By using iodides to precipitate the casein it should be possible to obtain, by sensitising in an acid bath, silver iodide pellicles suitable for chemical development; whilst the use of bromides would furnish silver bromide pellicles.

Casein stirred up in water can be dissolved in any weak acid by gentle heat, furnishing a hyaline, gelatinous solution. This solution poured over a glass plate, celluloid film, paper, or the like, while warm, will set on cooling and dry with a brilliant gloss. The dried film, which is still slightly soluble in water, may be floated or immersed in a solution of any metallic haloid, and thereby rendered insoluble, a sufficient quantity of the haloid salt for the formation of the silver haloid being incorporated in the casein stratum at the same time. Chlorides, bromides, and iodides, or mixtures of the same can be used in this way. The resulting stratum is as tough as leather, whilst permeable to liquids, and it can be rendered as flexible as desired by adding glycerine. It may be sensitised by a neutral or faintly acid solution of silver nitrate, inasmuch as this latter reacts on the metallic haloid in the stratum, to form the corresponding silver haloid. According as the casein has been fixed with chlorides or bromides, the product will be either a faintly sensitive chloride printing-out casein stratum or a highly sensitive bromide stratum suitable for development. The method, which is specially adapted for printing-out papers, is patented. These papers, which may be advantageously prepared by the aid of baryta, exhibit several valuable properties, which fill a long-felt want in practice.

They print fairly rapidly, in agreeable tones, and are easily toned in a sulphocyanide bath, which gives warm, pure tones, free from double toning. Neutral combined toning and fixing baths can also be used. Even in warm water the stratum remains tough and leathery, without softening, and it is perfectly flexible, so that the prints do not curl in the bath. The finished prints resist mechanical influences (scratching, rubbing, scouring, etc.) in a remarkable degree, and their sensitiveness to light is thoroughly good. The prints show soft, delicate gradation, somewhat softer and with finer definition than albumen prints, without exhibiting the hardness of gelatine or celloidin emulsion papers. Hence the casein papers combine in themselves the pictorial softness and the flexibility of the albumen papers, with the permanence and improved definition, together with the extensive range of toning methods enjoyed by the celloidin and gelatine emulsion papers, without the tenderness and susceptibility to temperature of the latter, either in the wet or dry state.

Even if papers prepared in this manner cannot be introduced into practice, the foregoing observations will serve to indicate the way in which the most readily available albuminoid, casein, can be utilised as a medium for photographic purposes.

Casein Ointment.—To prepare a drying ointment, pure, dry, pulverised casein is dissolved in a mixture of equal parts of dilute ammonia and glycerine. After heating the solution until the ammonia has been expelled, the solution may be mixed with fats to form an emulsion, which, when applied as an ointment to the skin, soon dries to an elastic, cooling layer.

Clarifying Glue with Casein.—According to Hewitt (New York), glue can be clarified by the addition of casein, which is afterwards thrown down by neutralisation (and heat, if necessary), leaving the glue perfectly clear, free from fat, colourless and inodorous.

Casein in Soapmaking.—The frequency with which casein has been offered for use in soapmaking has drawn the attention of interested parties to the matter, and led to exhaustive experiments to determine whether it is really suitable for this purpose.

In Austria the use of casein in soapmaking is protected by Letters Patent. The process is a development of the well-known milk soaps; and, just as an addition of cows' milk is considered to be an improvement in these soaps, so also, to some extent, is the use of casein in toilet soaps, since it can hardly be regarded as merely an adjunct designed to load or cheapen the product, except, perhaps, to a very restricted extent. From the practice of working up cows' milk into toilet soap to the use of casein for the same purpose is but a step. Then, again, it has been proved that toilet soaps containing casein have behaved better than those without such addition, and also that the casein added has a beneficial effect on the perfumes used, rendering their odour more pronounced and fixing them to some extent. Moreover, albuminoid washes have a beneficial effect on the skin, so that the use of casein seems commendable.

Casein being insoluble in water, it must first be brought into solution by combining it with alkalies such as borax, calcined soda, sodium bicarbonate or caustic soda.

In places where ample supplies of moist casein are available to the soap-maker, the method of incorporating it is fairly simple. The casein is placed in a pan fitted with stirrers, and dissolved in one of the aforesaid alkali compounds, with constant stirring, the solution being added to the finished soap.

To bring commercial dry casein into suitable condition for the same purpose it must be mixed with water containing the requisite alkali in solution. Casein thus treated will absorb large quantities of water, and it is on this property that its use as a method of cheapening soap is based. This applies more to curd soaps than to toilet soaps, especially when the Schnetzer moulding machine or the Klumpp cooling press is used. In the case of toilet soaps, *i.e.*, stock soaps for milled soap, such a large proportion of the moisture evaporates in the drying apparatus that the amount is reduced to about one-third, though it is still worthy of note in view of the other advantages presented by the use of casein.

As already stated, the casein is intimately mixed with the aqueous solution of alkali. The resulting, somewhat sticky mass, however, must not show an alkaline reaction towards phenolphthalein, though, nevertheless, all the casein must be in suspension. Even during this stage of the operation a strong smell of ammonia will be noticeable, and this increases when the mass is introduced into the hot soap. At the same time the liberation of carbonic acid is stimulated by the heat, therefore care must be taken that the soap does not rise and run over the top of the pan.

Another advantage of casein soaps is their greater lathering power, which is peculiarly desirable in the case of shaving soaps.

For these reasons Antony recommends all soap-makers to give casein a trial, since it will probably prove useful in some cases.

Casein-albumose Soap. — This soap is prepared from tallow and olive oil by saponification with a mixture of caustic soda and caustic potash. After salting-out with potassium chloride, a preparation of casein and albumose is incorporated with the soap, which is then superfatted to the extent of 7 per cent. This soap may be used in place of casein ointment.

Eberhardt and Mierisch's Soluble Casein.—A perfectly soluble, fat-free casein can be obtained by centrifugalising skim milk at about 104° to 113° F., treating it with caustic potash or soda, passing it through the separator again until no more fat is eliminated, and then precipitating the casein by means of an acid, *e.g.*, dilute sulphuric acid, or better still, by an acid forming soluble lime salts, such as ethylsulphuric acid, lactic acid or acetic acid. The precipitate is washed an dissolved in a solution of alkali. The entire process is then repeated several times, the casein being finally dissolved in ammonia, treated with benzine or chloroform to extract fat, and then filtered through diatomaceous earth or the like.

The resulting solution may be used *per se* or again treated with an acid to throw down the casein.

Waterproof Casein.—When a 5 per cent. solution of casein in alkali is mixed with formaldehyde no coagulation occurs, the solution remaining clear and fluid for a long time. If this solution be poured out on a sheet of glass, zinc, paper, etc., or left to dry, an insoluble film of casein is obtained.

Another way is to prepare a solution containing about 100 parts of casein and 1½ parts of caustic soda in 1,000 of water, to which 15 parts of a 40 per cent. solution of formaldehyde are then added. This mixture, which remains perfectly clear, is next poured out on a sheet of glass, zinc, or paper and evaporated or dried. In order to produce a waterproof film from an ammonia solution of casein, a solution is prepared containing about 100 parts of casein, and 10 parts of a 10 per cent. solution of ammonia, in 2,000 parts of water. About 30 parts of a 40 per cent. solution of formaldehyde are added, and the casein is dried as stated above.

This waterproof casein may be used in various industries, for instance, photography, papermaking and the preparation of surgical bandages.

CHAPTER XII.

CASEIN COMPOUNDS.

In view of the extensive general application of casein it is not surprising that many attempts have been made to obtain compounds of this substance with chemical elements, for a variety of purposes. In addition to those already described are a number of others, which, together with their mode of preparation, are given below.

To prepare compounds of casein with *iodine* the two substances are intimately mixed and warmed. The resulting products are used in medicine (German patent 79,926).

Dr. Bernstein prepares *albumose* and *peptone* from milk casein by bacterial agency.

Solid compounds, soluble in water, are obtained from casein with hydrobromic and hydriodic acids of medium strength by stirring the substances together; or by dissolving the casein in the dilute or concentrated acid (German patent 124,232, 1900), and precipitating the resulting casein compound. In therapeutic value these compounds are intermediate between the metallic bromides or iodides and the corresponding free acids.

According to J. Just's American patent of February 4, 1902, a casein phosphate can be prepared by adding to an aqueous solution of phosphoric acid a portion of the necessary quantity of casein, heating the mixture and concentrating it to syrup. The remainder of the casein is then added and well mixed with the mass, which is finally dried.

A *medicinal food* is prepared by the patent process of the Chemische Fabrik Rhenania, in which a solution of casein in very weak phosphoric acid is precipitated by a primary phosphate, the precipitate being freed from the excess of acid by washing with a solution of the same phosphate.

With *salicylates* casein forms soluble compounds, which are applicable in therapeutics owing to the readiness with which they are absorbed and the slight irritation which they cause to the mucous membrane of the stomach.

To prepare water-soluble compounds of casein with *alkaloids*, the latter—in alcoholic or other solution—are allowed to act on dry or moist acid-free casein.

According to Knoll & Co.'s patent, compounds of casein with an organic acid containing phosphorus and nitrogen are obtained by digesting casein with pepsin chloride, neutralising the filtrate with sodium carbonate, and treating it with iron-ammonium alum. On heating, the iron compound of casein separates out. This iron salt is soluble in the intestinal juices.

Soluble compounds of casein with *lithium salts* form the subject of a patent by C. Wendt, of Stollberg.

To prepare compounds of casein with heavy metals such as *mercury*, *silver*, and *iron*, solutions of neutral alkali casein are treated with salts of mercury or silver, and precipitated with alcohol or concentrated *in vacuo*. According to an additional patent of the Chemische Fabrik Pfersee, Augsburg, the albumen compound may also be suspended in alcohol or acetone and boiled with aqueous or alcoholic solutions of the heavy-metal salts. The mercury-, silver-, and iron-compounds thus obtained possess properties which seem to render them useful, both technically and medicinally.

Among the *silver* compounds of casein Röhmann and Hirschstein have discovered a product, which they term "argentumcasein". This is able to form salts and contains silver in complex combination, not as an ion. According to Imray's patent, a solid silver-casein compound of this kind, which does not furnish any precipitate when its aqueous solution is treated with albumen or salt, is obtained by mixing a solution of silver nitrate or other salt of silver with a neutral solution of an alkali casein, and evaporating the mixture to dryness *in vacuo.*

Compounds of *arsenic* and casein are prepared in the same way as those of the heavy metals, and are also used medicinally.

Alkali salts and the *potassium* salt of casein are obtained as dry powders by concentrating, *in vacuo*, solutions of casein in caustic alkalies, alkali carbonates, sodium phosphate or milk of lime.

The Casein Company of America (U.S. patent 717,085) prepares a casein compound which forms a thin solution with a relatively small quantity of water. This is effected by incorporating oxalates with casein, for instance, 2 parts of potassium oxalate and 15 of powdered borax to 100 of dry casein, the whole being thoroughly mixed.

A subsequent patent relates to the production of *oxidised casein* by dissolving an oxidising agent in about its own weight of water, and then rapidly stirring in the casein to ensure intimate mixture. Ammonium persulphate is the oxidising agent preferably used. Oxidising agents, however, cause more or less decomposition in casein.

An *insoluble casein compound* is prepared, according to B. Dunham's patent, by mixing about 15 parts of borax and 85 of commercial casein, dissolving this in 400 parts of water, treating the solution with about 15 parts of hexamethylene-tetramine and leaving the liquid to evaporate, the dry product being then exposed to heat and moisture. The preparation is suitable for replacing egg albumen.

Kalle & Co. (Biebrich) have patented a process for preparing compounds of *Acrolein* with starch, dextrin, gums, or proteids, *e.g.*, casein, for therapeutic purposes.

Casein acts as a weak acid forming salts which are neutral toward phenolphthalein, but alkaline towards litmus. By Liebrecht and Röhmann's patented process not only are these neutral lime and sodium compounds prepared, but also solid casein compounds of alkalies and alkaline earths, with an acid reaction. For this purpose the acidity of the casein is first determined with phenolphthalein. To prepare a neutral compound the casein is dissolved in the calculated quantity of alkali; for an acid compound half the quantity is employed, and the solution concentrated *in vacuo*. The resulting neutral compounds are well adapted for painting, whilst the compounds acid to phenolphthalein are of special importance for dietetic and similar purposes.

L. L. Van Slyke and E. B. Hart[1] prepared pure casein almost free from mineral matter by precipitating with an acid and repeatedly washing with water. This product became plastic on warming and readily dissolved in a 5 per cent. solution of sodium chloride, and also in 50 per cent. alcohol on warming. From this casein a basic calcium-casein was prepared containing 2·4 per cent. of lime and also a neutral calcium-casein containing 1·5 per cent. of lime.

Paracasein free from bases was also obtained by adding ammonium oxalate to skim milk filtering, acting upon the filtrate with rennet for two hours and then precipitating with hydrochloric acid. The product was dissolved in lime water, and from the solution basic calcium-paracasein, containing 2·4 per cent. of lime, and neutral calcium-paracasein, containing 1·5 per cent. of lime were prepared. These compounds also dissolve in a solution of common salt and in 50 per cent.

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[1] "New York Expt. Stat. Bull.," 1905, **26**, 1-37.

alcohol, and are regarded by the authors as identical with the casein compounds.

The *ammonium* compound and the *hydrochloric acid* compound of casein can be prepared (German patent 84,682) direct in the solid form by passing gaseous ammonia or hydrochloric acid over finely powdered dry casein ; or by suspending the latter in some liquid (*e.g.*, alcohol, ether, ligroïn or benzol) in which it is practically insoluble, and treating it with one or other of the above-mentioned gases. The resulting compounds are in the form of white powder, stable in air, and dissolve to a clear, almost tasteless, solution in water.

The feature of Dr. Dojen's process for preparing a compound of casein and *formaldehyde* is that pulverised casein is digested with formaldehyde, then dried, treated with dilute caustic alkali and digested for a long time at ordinary temperature with a concentrated solution of formaldehyde. The product has the bactericidal properties of formaldehyde without its irritating action.

According to German patent 98,177, a dilute aqueous solution of sodium or other *glycerophosphate* is mixed with an excess of casein at a temperature of 30° to 40° C. ; and after standing for twelve hours, the filtrate is concentrated *in vacuo* at 40° to 50° C.

THE END.

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