Terpineol nitranilide was made from the nitrosochloride and aniline dissolved in alcohol. On dilution of the reaction mixture with a little water good crystals of the nitranilide were obtained.

Dehydration Products.—Wallach[1] found that when 25 grams of terpineol were heated with dilute sulphuric acid, there resulted 16 cc. terpinene and cineol boiling at 177–180°, 4 cc. boiling at 181–185°, and 1.5 cc. boiling at 185–187°, containing terpinolene. This experiment was repeated, using a sample of long leaf pine oil, of which nearly the whole distilled at 216–218°. 100 grams of this oil heated for one hour with 400 cc. of dilute sulphuric acid (1 : 2) and then distilled with steam and dried over sodium, gave 85 cc. of oils volatile with steam. On redistillation the following fractions were obtained: 5 cc. at 165–175°, 56 cc. at 175–180°, 6 cc. at 181–185°, and 15 cc. at 186–192°. The largest fraction had a specific gravity of 0.860 and evidently consisted essentially of terpinene. It will be seen that these results agree quite closely with those obtained by Wallach from pure terpineol.

In conclusion, the specific gravity, index of refraction and boiling point of the long leaf pine oil, its absorption of bromine in quantity corresponding to a dibromide, the formation of a nitrosochloride, nitropiperidide and nitranilide, the formation of terpinene by dehydration and the easy conversion and large yield of terpin hydrate leave little doubt that the essential constituent of long leaf pine oil is a terpineol and is probably the optically active levo modification of α-terpineol (Δ'-p-menthenol(8)) boiling at 217–218°.

This seems to be the first recorded occurrence of terpineol in any member of the pine family. Even in this case it was obtained not from the living tree but from lightwood, *i. e.*, from portions of the tree which had been cut at least three years and were very resinous. It is the common belief of those familiar with lightwood that its resinous content increases regularly from the time it is cut from the tree or from the death of the tree. If any such action occurs the appearance of terpineol here would seem quite natural, as its formation from pinene requires only the addition of one molecule of water accompanied by splitting the tetra ring of pinene.

The investigation of this oil is being continued.

164 FRONT ST., NEW YORK CITY,
December, 1907.

TRANSPARENT SOAP—A SUPERCOOLED SOLUTION.

BY W. D. RICHARDSON.

Received January 15, 1908.

The alkali-metal salts of the fatty acids—commonly called soaps—have been usually considered crystalloids by the older authorities and by others in recent years as colloids.[2]

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[1] Wallach, Ann., **230**, 225.

[2] Leimdorfer, Seifensied. Ztg. **1906**, Nos. 24-29; Merklen, Chem. Abs. **1907**, 2416; Lewkowitsch, J. Soc. Chem. Ind., **26**, 590 (1907).

The criteria of colloids are: (1) slow or no diffusion through colloidal membranes; (2) failure to raise the boiling-point or lower the freezing-point of solvents; (3) electrical migration; (4) coagulation phenomena; (5) absorption phenomena; (6) hysteresis; (7) impenetrability for other colloids; (8) optical inhomogeneity; (9) separation by salts ("salting out"). Of these criteria at least (2), (5), (7), and (9) hold good for soap.

It is probably true that many facts in regard to the formation of soap and also many properties of finished soaps can be explained on the assumption that they are colloids forming in solution reversible hydrosols in the classification of Zsigmondy,[1] but it is equally true that they crystallize, if not quickly, at least slowly and definitely. In all likelihood the ordinary pure soap of commerce consists chiefly of a compact mass of soap crystals embedded in a non-crystalline soap phase. A thin section of such a soap transmits light through crossed Nicols and while this phenomenon can be explained upon other assumptions, the facts of opacity and the presence of straight line boundaries indicate the presence of masses of crystals. Possibly the best view to take of the matter would be to consider soap as a substance with distinctly crystalline tendencies, which on account of the size of its molecules, its viscosity and its solubility, which varies considerably with the temperature, exhibits colloidal properties.

In cold water many of the alkali metal salts of the saturated higher fatty acids are but sparingly soluble, whereas at temperatures under 100° and ordinary pressures, solutions are readily formed consisting of 70 to 80 per cent. of soap and 30 to 20 per cent. of water. These solutions are quite transparent, but upon cooling they become opaque. The opacity of some soaps is in part due to the presence of an emulsion of soap and fatty matter, and this is well illustrated in the case of cold-made soaps, in which saponification is purposely left incomplete; but in the instance mentioned the opaque mass is formed of pure soap and water.

A soap may, however, be of such a composition that when it solidifies, instead of becoming opaque, it remains clear and such a soap is known in the trade as transparent soap. A familiar example of such a product is a cooled alcoholic solution of soap. This, upon solidification, assumes the appearance of a jelly and if not perfectly transparent is at least translucent. A solidified dilute water solution of soap is also frequently translucent; but whether the jelly be made with alcohol or water, soap crystals of rather imperfect shape usually form in time. It may be said in passing that transparency in soap is not a mark of purity or even of definite composition. Probably a better soap can be made of the ordinary opaque sort. The best known brand of transparent soap on the market contains 20 per cent. of rosin, calculated on the basis of total

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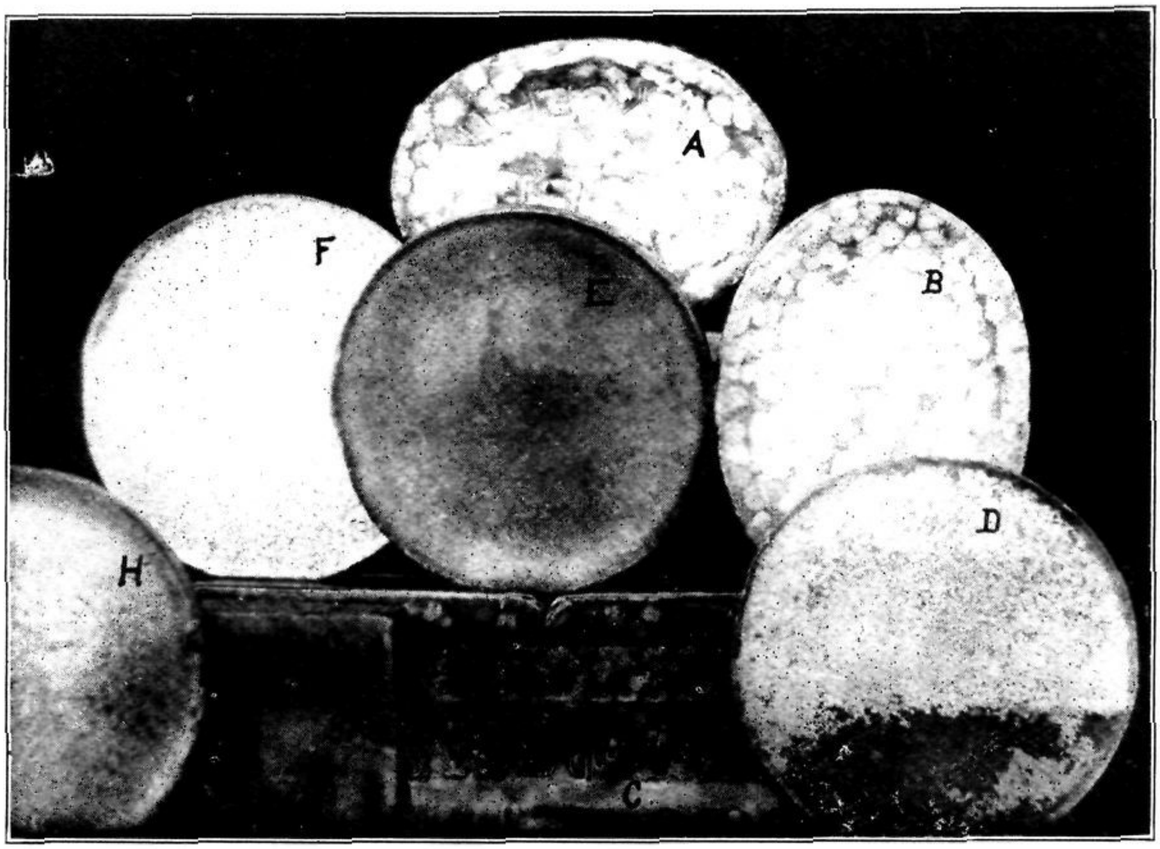
[1] Zsigmondy, Zur Erkenntnis der Kolloide.

acids, and rosin must be considered as an inferior soap-making material. The demand for a transparent soap must be attributed to a whim of that portion of the public to whom transparency is synonymous with purity.

In commercial transparent soaps there are usually present one or more substances which appear to act as retarders, preventing crystallization. Among these substances are glycerol, ethyl and methyl alcohols, cane sugar and alkali-metal salts of rosin. Also certain soaps (such as the sodium soap of castor oil) seem to have this power. While some of these substances, at least under certain conditions, maintain the soap in a transparent state by means of a considerable solvent power, in other cases they appear to act simply as retarders, preventing or hindering crystallization. In mentioning retarders, the action of certain substances, such as protein substances boiled with lime water, upon the setting of plaster of Paris might be cited. One part of retarder to one thousand of plaster may retard the setting time an hour or two; large quantities will retard it an infinitely long time. Such seems to be the action of some of the substances mentioned upon the crystallization of soaps. Retarders act in another way also (since some are hygroscopic) by prevention of too great desiccation under ordinary circumstances and, therefore, by preventing the soap from assuming the supersaturated condition. Thus some transparent soaps which would never form crystals when exposed to the air, do so when kept in a desiccator over calcium chloride or sulphuric acid. When removed from the desiccator and placed in a moist chamber the soap swells, absorbs water and the crystals in time dissolve. The same soap, returned to the desiccator, may not form crystals the second time.

It is ordinarily stated in text-books that there are two ways of preparing transparent soap; one by dissolving dry soap in alcohol, distilling off the alcohol and moulding the syrupy residue; the other by "filling" molten soap with sugar, syrup, etc. As a matter of fact, there are not two but many ways of manufacturing transparent soap, but the principle in all cases is essentially the same, namely adding to a soap solution substances which will form a jelly and retard crystallization. Pure soap, when dissolved in alcohol and the alcohol distilled off entirely or in part, will form not a transparent soap, but an opaque one. If the 20 per cent. of rosin were left out of the brand for which the first process mentioned above is claimed and if no glycerol were present, it is questionable whether or not a transparent soap would be the result. One formula for transparent soap commonly given in the literature is:

Tallow	100	parts
Cocoanut oil	100	"
38° Bé. caustic soda solution	150	"
Glycerol	40	"
Alcohol	80	"



EXPLANATION OF PLATE.

A, B and C, cakes of transparent soap containing naturally occurring soap crystals; A and B contain many disc-shaped crystals, C fewer. D, E, F and H contain crystals which have been formed by seeding molten soap with crystal fragments from A and B. In the lower part of D is an area where crystals have not formed, probably owing to absence of nuclei. G is a bar in which a rod of soap containing crystals, cut from C by means of a cork borer, has been inserted and from which crystals have grown, although they do not show well in the illustration.

This formula does not make a transparent soap but a decidedly opaque and crystalline one. One hundred parts of castor oil and the necessary caustic soda may be added besides, the glycerol and alcohol may be trebled, but the product is still opaque. If now rosin soap is added or cane sugar, or both, a perfectly transparent soap results.

As transparent soap comes from the kettle it is quite clear and transparent; after solidification in frame or mould it is usually, though not always, less clear. After partial desiccation it becomes quite transparent again to the eye, when viewed with ordinary light, although it probably diffuses light to some extent. Immediately after manufacture transparent soap does not transmit light between crossed Nicols but with age this property increases until finally, when viewed even in thin sections, a soft bluish light is transmitted by such soaps of the most varied compositions. It is the usual rule with transparent soap that after aging it reaches a condition after which no great change ensues; the bars remain transparent and firm and do not lighten or darken in color. But occasionally soap crystals form in a bar which is in all visible respects like the normal bar; further, these crystals may form in a bar of identical composition with one free of crystals; the bar with crystals and the one without may indeed have come from the same batch of soap or the same frame. The crystals when first visible are about one-half millimeter in diameter; they may enlarge until a diameter of fifteen millimeters is reached. When one millimeter in diameter they appear under the microscope in section as fine needles radiating from a center, which is somewhat opaque, into a clear matrix. Between crossed Nicols the appearance is striking. The central portion transmits light in a marked manner and appears red and yellow; surrounding the central portion in a circle of bluish light; surrounding this and reaching almost to the crystal-needle ends is a black ring. Just outside the crystals is a bright bluish ring; this is in the transparent region and beyond this is the uniform dim bluish area characteristic of the non-crystalline soap. The outer bright, bluish ring would appear to indicate a condition of unusual strain in the soap. The crystals usually become noticeable in from four to eight weeks and they grow in size and numbers for an indefinite time, depending on conditions. Sometimes they appear in as short a time as one week and again they may not become visible for from eight to ten months. In some cases only a few crystals develop, in others the bar finally appears as a mass of soap crystals lying in a clear matrix. Attempts have been made to separate the crystals from the matrix by solution in hot and cold alcohol and water and other solvents, but unsuccessfully, although the crystals differ to some extent in their physical behavior from that of the transparent portion of the soaps. The crystals have been separated by hand in small quantities by excision, and their analysis indicates their composition to be that of ordinary pure soap. The amount of material thus separated was small and probably impure, owing to the fine needle form of the crystals and their ramifying tendency. The fatty acids were separated from them as well as from the clear matrix surrounding them and melting-point determinations made upon the acids. Those from the crystals melted at 43–44°, while those from the clear portion melted at 36–38° C. These figures establish little beyond the fact that it is the soaps of the harder fatty acids which form the crystals and that these soaps are probably composed of saturated acids, for the melting-points of unsaturated fatty acids are low.

The facts indicated above, that crystals form in one bar of soap and not in another when both are from the same batch and that the introduction of soap crystals leads to the formation of crystals in otherwise non-crystalline bars, would lead to the conclusion that nuclei of some sort are one of the essentials leading to crystal formations. There is another fact of interest in this connection, namely that crystals are frequently formed abundantly in the interior of a bar whereas the surface to a depth of from two to six millimeters is free from crystals. It is apparent that this condition is connected with the progress of desiccation in the cake, for the line of demarcation between well dried surface and moister interior corresponds closely with the boundary between crystalline and non-crystalline soap. The surface of soap dries quickly to a depth of about one millimeter, but thereafter the desiccation is extremely slow, inasmuch as the surface skin so formed protects the interior against the loss of moisture. The dried portion is very hard and tough and consequently possessed of great viscosity and rigidity. In such a medium, even though it be supercooled, crystal formation is almost, if not quite, impossible.

I have used the term "supercooled" in referring to transparent soaps rather than "supersaturated," because the substance is in the solid condition, is amorphous and may start to crystallize at once upon solidification from the kettle without any evaporation of the solvent. While there may be a slight impropriety in the use of the term, it appeared fully as useful in describing the properties of the soap as the term "supersaturated."

Now the characteristic of the supercooled or supersaturated condition is its instability as regards crystallization. The means sufficient for bringing about equilibrium are shock, or the introduction of a like or isomorphous crystal. Viscosity or rigidity in an amorphous substance may render crystallization extremely slow or prevent it altogether. For example, the devitrification of glass is usually a very slow process.

If a soap crystal be introduced into a bar of transparent soap and if the solvents are not present in excess (that is, if the soap is indeed in condition for crystallization) radiating crystals will start to grow from the one introduced and will spread to an indefinite extent through the soap, if sufficient time be allowed. If soap crystals be ground in a mortar and ever so small a weight of them be introduced into transparent soap as it is about to solidify, the soap will in time become a mass of crystals. If, on the other hand, the same weight of soap crystals be dissolved in a small quantity of alcohol, and this solution added to the molten transparent soap, and if the soap be then filtered as a special precaution against the introduction of nuclei, no crystals will form. In one series of experiments holes were made by means of a cork borer in bars of transparent soap, which contained no crystals, and into these holes, plugs of soap cut from a crystalline bar with the same cork borer were pressed. Around the plugs so introduced masses of crystals formed and are still forming, although some of the experiments are now a year and a half old. In the parts of the bars remote from the crystalline plug no crystals have formed at all. Not all nuclei induce the formation of crystals. For instance, in one series of experiments particles of crystalline silica were incorporated in molten soap, and these, during one and one-half years' time, developed no crystals, although soap of identical composition, when seeded with soap crystals, produced a large crop. Experiments on various substances as nuclei are now in progress.

The influence of shock or physical strain in the production of soap crystals is shown by the tendency of the crystallization to proceed in certain planes which follow the lines of strain produced in the soap by the impress of the die used in stamping the bars. This produces crystals, in the form of circular discs (of radiating needles) rather than spheres; also the crystals near the surface frequently cluster around a line or edge where the die has struck, rather than against a plane surface of the soap.

It will be seen that no one explanation will account for the formation of crystals in transparent soap under all conditions. The inertia or hysteresis attending change of state may be accentuated or retarded in this case as in others by a variety of circumstances. The principal influences and conditions affecting the formation of crystals may be grouped as follows:

(1) Supersaturation or the supercooled condition presupposing a condition of strain.

(2) Absence of sufficient quantities of retarders to prevent crystallization altogether.

(3) Desiccation: provided the soap is not supersaturated at the time of manufacture, desiccation is necessary to bring about conditions suitable for crystal formation. As desiccation proceeds there is apparently an increase in strain produced in the soap as shown by the transmission of light between crossed Nicols.

(4) Nuclei appear to be the principal exciting cause of crystal formation when other conditions are favorable. These nuclei are soap crystals or particles and possibly other substances. Experiments are now in progress in regard to this point.

(5) Not too great viscosity or this may overcome the crystallizing forces. Rapid desiccation may entirely prevent crystal formation.

(6) Shock produced by blows or pressure act favorably on crystal formation in many cases.

In conclusion, crystal formation, while it does not reduce in any degree the detergent power of a soap, renders it more or less unsalable to a public which buys according to the appearance of goods. The experimental work detailed above was undertaken in order to examine systematically the causes of crystal formation in transparent soap and to provide a remedy.

CHEMICAL LABORATORIES OF SWIFT & CO.,
CHICAGO.

NOTES.

Rapid Determination of Petroleum Naphtha in Turpentine.—To determine the amount of petroleum naphtha in a suspected sample of turpentine, 10 cc. are carefully measured into a 50 cc. carbon tube, which is graduated into tenths of a cubic centimeter.

Thirty cubic centimeters of aniline are now added and the mixture violently shaken for five minutes, and left to settle until the liquid has become perfectly clear, when, if there is any petroleum naphtha present in the turpentine, it will be thrown out of solution and float in a layer on top, and the percentage can be readily ascertained. I get excellent results from this method, but care must be exercised that the aniline does not contain any water. HENRY C. FREY.

2521 REYNOLDS ST.,
BRIDESBURG, PHILADELPHIA, PA.

Determination of Sodium and Potassium in Silicates.—We have found the following method of determining sodium and potassium in clay and silicates which can be decomposed by sulphuric and hydrofluoric acids, rapid and satisfactory.

One gram of clay is decomposed by means of sulphuric and hydrofluoric acids, and the excess of sulphuric acid expelled in a hot air bath. The residue is then dissolved in water and powdered barium hydroxide added to the boiling liquid to alkaline reaction. The solution is decanted and filtered and the residue boiled again with water and thoroughly washed. Carbon dioxide is passed into the filtrate in excess, the solution evaporated to 50 cc., 25 cc. of alcohol (96 per cent.) added,