COLLOID DEVELOPMENTS IN SYNTHETIC RESINS

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Industrial resins are essentially organic glass-like mixtures which melt and flow at sufficiently low temperatures to enable reinforcing with a great variety of materials. They are alike in having great strength when in thin sections, that is, when approaching molecular thickness of films, but differ progressively from some resinous mixtures having fair strength in massive form to others having comparatively low massive strength. They may be brittle, may lack shock resistance, may be of low tensile strength as a mass, and yet may exhibit great strength when used as an adhesive between two surfaces, for instance, between two particles of wood. The essential factor then of the resinous field is the great increase in strength as the plastic flows and hardens in sections of near-colloid thickness.

This resinous plastic field may well be divided into two main divisions dependent upon properties which find reflection in use. (1) The *resins*, which are melted for flow and cooled for hardening into the finished shape. These are generally called thermoplastic resins and include natural resins, the resin esters or ester gums, the cellulose esters and ethers, and a great many synthetic resins, as the novolak phenol–aldehyde resins, the glyptal resins, the vinylite resins, etc. (2) The *resinoids*, which in molding are heated for flow and also heated for hardening effect. These include the original heat-hardening phenol–formaldehyde resinoids of Baekeland and their many modifications, the urea–aldehyde resinoids, and some of the glyptal type.

The concepts of film formation, adhesion, surface tension, etc., are perhaps common to the above two groups; the two groups differ sharply in permanency of plasticity and in the importance of particle size effect on properties.

Resinous compounds and their mixtures differ from crystalline compounds in the capacity for plastic flow at temperatures below a true melted condition as contrasted to the sudden transition from a rigid condition to the limpid liquid flow of melted crystals. This property of plastic flow with heat naturally leads to analogy with the fields of metal, glass, and rubber. These fields, being older and easier to study, have to date given us the more valuable colloid data bearing on the resin field. For example,

present empirical resin formulas take advantage of the ability of resins to temper like glass and metals, and to stiffen and strengthen like rubber with the incorporation of small particles. Yet such general data need better assembling and classification so that they can find their true sphere of use in the resin industry.

Data for the resin field might well be divided into three groups: (1) Flow, or plasticity, which deals with the resin mixtures in motion and with resistance to flow. (2) Rigidity, set, or hardness, which deals with a static condition or total resistance to flow. (3) Colloidal surface effects, or distensibility both of portions within the mass and of the mass as a whole distributed over added particles.

Plastic flow is a universal property of matter and dependent only upon the pressure exceeding a definite yield value. Thus the familiar collapsible metal tube for tooth paste may be cold-pressed to shape and even steel cold-drawn into seamless tubing. Reiner (38) says that every material flows under certain conditions and refers to Karman (24), who described cubes of marble flowing under sufficiently high pressure as behaving under those conditions like any plastic substance. The problem in plastic materials then is not just to make materials flow but to control the flow of certain adhesive materials under available commercial pressures.

We see that plastic flow involves mechanical work, so we are induced to consider applied force in different ways: first, as the cause of controlled plastic flow; second, as the cause of changes in plastic flow values; and third, as will be explained later, as a cause of certain definite changes in physical properties.

In the resin plastic field properly controlled plastic flow is obtainable as follows: (1) by choice of resinous material; (2) by choice of filling materials, both coarse and fine; (3) by fineness of grinding of the solid mixed mass with a proper balance of fine and coarse particles; (4) by processing the resin to proper plastic flow range, as by means of polymerization, by distilling off liquid products, or by addition of plasticizers; and (5) by the use of solvents or temporary plasticizers.

For the use of coarse filling materials we have Baekeland's (3) original rule: "Judicious incorporation of fibrous substances provides increased resistance to shock in the final heat-hardened product."

For the use of colloidal filling materials we find data available in the rubber field. Rubber, under proper conditions, fulfills all the essentials of resins. Except for the fact that rubber has grown into an immense special flexible field of its own, the resins and rubber fields might be classed as a unit.

We shall consider later the definite resinous properties of rubber, but we are here concerned with the availability of data concerning additions of

small-sized particles.   Endres (14) has shown the effect of particle size of barium sulfate from colloid size up to gross size.   He found an increased stiffening and strengthening effect with decrease in average size.   Apparently the effect reaches a maximum such as Alexander's (1) "zone of maximum colloidility," since this effect is known to disappear again when we reach the realm of dispersed molecules.

Polymerization in a mass at rest is often a very different phenomenon from that of the same mass when in motion.   Polymerization is the term we use to denote change of a substance without loss or gain of material but generally, with a transfer of energy, to a less soluble, less fusible, less chemically active form of higher average molecular weight.   We have many examples both of easily reversible and of so-called irreversible polymerization.   Naturally the most complete data has been published in the field of reversible polymers.

Staudinger (46) has many papers on the polymers of styrene, some forms of which are controllable and reversible.   He may be considered the foremost exponent of a micellar structure as formed from primary valences, just as Meyer (35) expounds the merits of the secondary valence or association theory, and Bergmann the theory of coördination in the solid state of units incapable of free existence.   All the various theories of polymerization are intensely interesting, but the known facts are even more interesting.

Any simultaneous lowering of flow, lowering of solubility, raising of melting point, and raising of average molecular weight is by definition polymerization.   We at present suspect that this broad definition may cover two distinct classes of phenomena: (1) Change in particle or molecular size, generally resulting in higher average size but not necessarily higher maximum size.   (2) Rearrangement as to particle or molecular position, that is, a change in average directional influence.

Staudinger (47) has given us some very valuable suggestions as to long slender chains of monomeric groups linked together by primary valence bonds.   Length of the chain forms his distinction between hemicolloids and encolloids.   The short chains of a hundred molecules or so are said to be stable to heat treatment when in solution, whereas the longer (and reversible) encolloids of some thousand molecules often lose viscosity by heat treatment.   Solutions of these long fiber molecules form films which are like mats of macrofibers and are tough and strong from their interlocking structure.   Thus from styrol at elevated temperatures, hard, brittle masses were obtained of comparatively low molecular weight, while from long-time reaction at low temperatures, tough masses were obtained which were more flexible and had average molecular weights four or five times as large.

We have found that the picture as drawn by Staudinger from reversible polymers cannot be indiscriminately used in the heat-hardening field. At any temperature, solutions of resinous particles of the heat-hardening type show the effect of conflicting forces, various ones of which predominate at different times and under different conditions. When one suspends solid resinous particles in a solvent, one expects a change in viscosity until a stable condition is reached. In the case of synthetic resinoids one notices a swelling of the particles, followed by dispersion with a drop in viscosity. If a condensation or polymerization reaction is progressing at the temperature of test, one then may expect a gradual rise of viscosity with time, the measured viscosity at any instant being, of course, the resultant of those several forces. When the resinoid is heat-hardened in the presence of the solvent, the swelling and dispersion phenomena may be eliminated from consideration and we should expect a gradual rise of viscosity. This is a beautiful theoretical picture, but the fact remains that almost all such resinoid solutions show a sudden and sharp viscosity drop, which may be completed a few minutes or hours after cooling to room temperature.

Since these changes are rapid and nearly always complete by the time a still charge is ready for shipment, they were ignored until by accident we found formulas in which the changes were prolonged sufficiently to interfere with commercial use. In figure 1, curves A and B are the changes in viscosity with age of two commercial rapid heat-hardening phenolic resinoid varnishes. Curve D shows changes of an experimental slow type flexible phenolic resinoid in one solvent, and curve C shows the changes of the same resinoid as in D, but in a mixture of solvents.

In this class of resinoid solutions we find, as also was found by Carothers and Hill (7) in the resinous ester field, and contrary to Staudinger's theoretical concepts, that high temperature favors high viscosity and low temperature favors low viscosity. Perhaps as yet no general rule can be drawn. We had the case of a solution which having been heated to 3000 centipoises at 95°C., then cooled to 25°C., dropped in four weeks to 500 centipoises. At the end of a year it tested 600 centipoises. The next surprise was to find resinoid solutions showing unstable viscosity at constant temperature, the fluctuations occurring between non-flowing gels and low viscosity liquids over constant and reproducible cycles as shown by the curves in figure 2.

Some changes in plastic flow phenomena occur in raw rubber when it is "racked," that is, pulled into a thread at any temperature and held rigid by excessive cooling under stress (17). On again being heated the rubber will retract at a temperature which bears a definite relation to the temperature at which stretching occurred. Bary and Hauser say that rubber

consists of two polymers, α-rubber and β-rubber, the β-rubber being the less soluble. X-ray examination of "racked" rubber shows that the
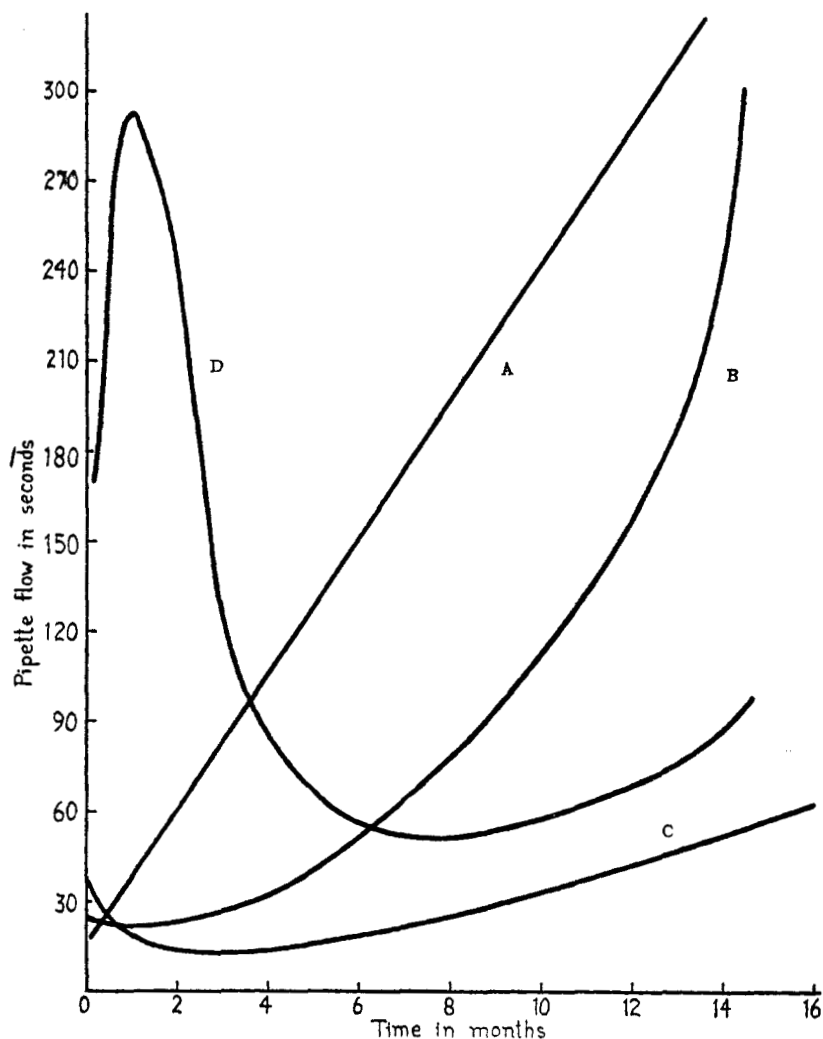

FIG. 1. VISCOSITY CHANGES IN SOLUTIONS OF RESINOIDS STANDING AT ROOM TEMPERATURE

A, commercial phenolic–formaldehyde resinoid varnish; B, rapid hardening phenolic resinoid solution; C, flexible mixed phenols–formaldehyde varnish in mixed solvents; D, same resinoid as in C, but in a single solvent.

change from α- to β-rubber can be followed in the racking process, with the probability that the β-form is in a more highly aggregated condition (4).

Since the racking of rubber turns it temporarily into a resin-like compound, the data become of great importance in the resin field.

The data by Gibbens, Gerke, and Tingey (17) shows that for racking temperatures above 20°C. there is a fairly uniform difference between the
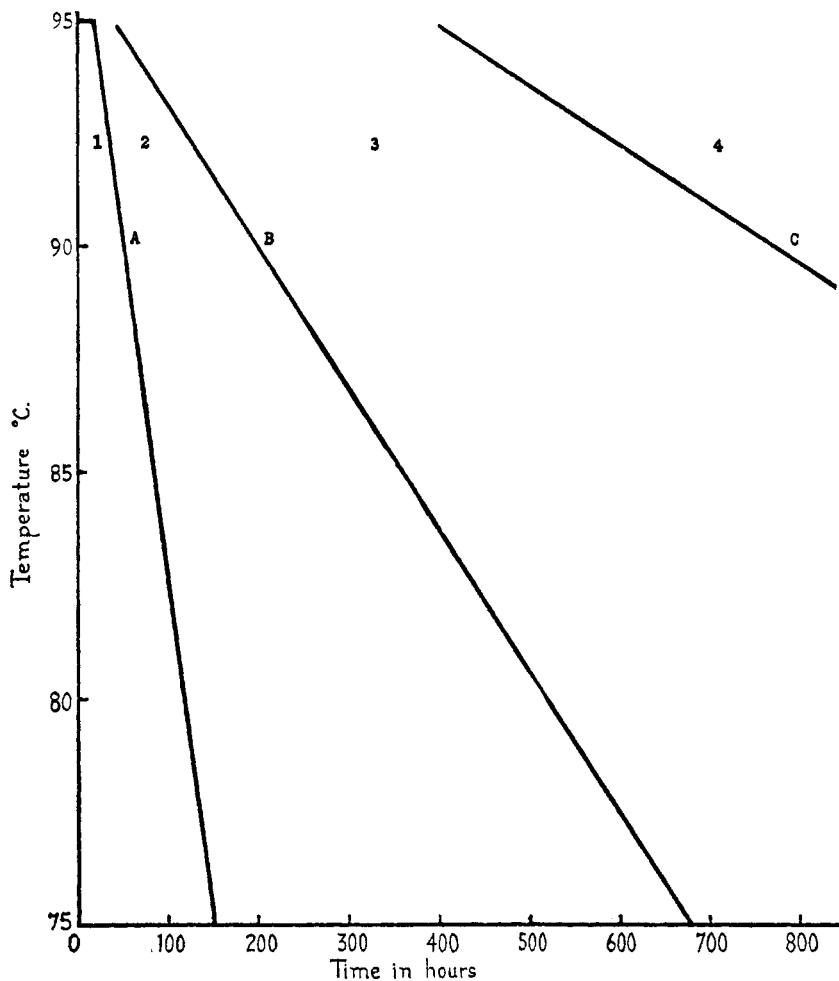

FIG. 2. GELATION CHANGES OF PHENOLIC RESINOID SOLUTIONS

A, time of gelatin of XH-1383 (60 per cent phenolic resinoid solution); B, time of reliquefaction of XH-1283 solution; C, time of regelation.

1, first liquid state; 2, first gel state; 3, second liquid state; 4, second gel state.

racking and the retraction temperatures. This temperature difference may be a measure of the molecular or micelle rearrangement resulting from the mechanical stretch.

A glance at the properties of "racked" rubber as compared to "unracked" rubber will indicate that we are here dealing with a reversible polymerization change induced by mechanical work. "Racked" rubber has increased in density (15), has taken on a fibrous structure (20), has increased in melting point (15), has increased in breaking strength, has become hard and inelastic, has given up heat, and has become of lower solubility.

α-Rubber and β-rubber are considered as different polymers of rubber hydrocarbon modified perhaps by natural proteins, resins, etc. In this connection it is interesting to note that pure rubber hydrocarbon when crystallized exists as fine needles (42). On the other hand, rubber goes to a resin-like product when heated in air with catalysts present (13).

All high-melting resins and some non-melting resins approach a rubber-like state at elevated temperatures. Rubber itself is a hard brittle body at very low temperatures. Rubber then might be considered as a fortuitous case of having elastic properties at room temperatures.

Autopolymerized styrene at temperatures above 65°C. behaves essentially as does raw rubber at room temperature. Thus above this temperature range the styrene polymer may be "racked." It then shows elastic set and elastic after-effects, as disclosed by Whitby and coworkers (50).

Another known effect of mechanical work on plastic flow may be found in the studies by von Weimarn (48) of natural silk dissolved and precipitated from solution. He has proposed the descriptive phrase "coagulation by motion."

von Weimarn dissolved (disintegrated) natural silk, then coagulated and dried the coagulant. Instead of a flexible substance like silk he arrived at a brittle resinous "glass-like" mass. When the wet mass was pulled into threads, using one simple pull, and the relaxed thread then dried, a brittle thread of low strength was obtained. However, when the thread was stretched and allowed to relax several times before drying, much stronger threads were obtained. From this discovery it was but a step to finding the mechanical working conditions which give silk threads a degree of strength far surpassing that of natural silk.

This concept of strengthening fibroin into silk thread is an exceedingly interesting one, especially when we note that the silk worm stretches and manipulates the secreted fibroin and that such stretching causes it to congeal rapidly.

To designate the concept of increased strength as derived from motion resulting from externally applied force we shall for convenience use the term "fibration." Thus natural silk is said to be "fibrated" fibroin. This concept of silk as a "fibrated" or rearranged resin will in time both explain many phenomena in the silk field and lead to better understanding in the resin field. Consideration of "racked" rubber and "fibrated" silk will

explain empirical data in the resin field, and perhaps systematic search will lead to many resins which can be "fibrated" to flexible threads or "unracked" to rubbery masses.

Carothers and Hill (8) produced high molecular polymers by the reaction of dibasic acids and dihydric glycols. They assume a theoretical completeness of this reaction series when all the initial reactants have united, into one single massive molecule with a progressive loss of water. When these reaction products reach an apparent molecular weight of around 9000, they are generally resinous in properties. Certain of these high molecular weight products exhibit the peculiar property of a temporary plastic flow which Carothers (9) has characterized as "their capacity to be drawn out into very strong, pliable, highly oriented fibers." That is, in the preferred terminology these products can be "fibrated." They disclose that a hot-drawn or extruded rod of these resinous materials is opaque, brittle, and resin-like, but if the same be subject to tension at lower temperatures, it will undergo a limited amount of flow and then, as an effect of this motion, will build up resistance to flow, that is, as we say in the plastic field, it will harden or congeal. These rods are therefore rendered less plastic by tension. By flow they have been transformed from an opaque to a transparent mass of high luster. They have increased greatly (about 600 per cent) in breaking strength and in pliability. The final strengths obtained were about equal to the values for cotton fiber.

Von Weimarn found that the rearrangement in fibroin could be followed under the microscope. The "fibration" proceeds from the outside towards the center with increased mechanical manipulation.

Some changes of properties with mechanical work are well-known for many compounds and mixtures. For instance, ordinary gelatin–water mixtures decrease in viscosity on stirring, so much so that in ice cream laboratory technique the "basic viscosity," defined as the minimum obtained on stirring, is reported (36). The viscosity of resin solutions and certain properties of solid resins, such as melting points, are also subject to the same type change with mechanical agitation, and this fact must often be considered to avoid confusion of data.

In weak gel-like solutions of these amorphous materials we note two conflicting influences. (a) That which is commonly called "thixotropy" (25; also 43) is the gel property of being easily broken with agitation and of reassembling on standing. (b) Rearrangement to a flexible condition within the gel. This last is of considerable interest and is not so well-known.

A dilute ammonium oleate solution is a weak gel when standing; Seifriz (39) prepared a solution with a viscosity to just support a 10μ nickel particle. With mechanical agitation this solution assumes a very highly

elastic state. On cessation of rotary stirring, air bubbles may be withdrawn backward as much as 180°. When quiet and measured immediately, it shows a viscosity to support a nickel particle forty-five times as large as before agitation. This elasticity, however, is gradually lost on standing and finally reaches the former quiet value of 10. The process may be repeated many times with the same solution. Threads of this ammonium oleate gel may be stretched several inches.

In addition to the disruption of gels and the temporary strengthening of gels we also note that sols have been coagulated by stirring (16, 37).

Laszlo (28) considers that shellac, distyrene, and rubber are all two-phase gels, and that even hard glass-like resins may be jellies built up from and containing both liquid and solid constituents. If the hard resins are jellies we should then by analogy also find in them all of the above effects of mechanical work as are known to change the properties of gels, namely: (1) change of plastic flow, both loss and gain, as the result of motion; and (2) change of other properties as the result of motion.

The curves of various resinoids in figure 3 show the breaking-down effect of the resin structure under milling conditions as being typical for gel structures.

It is well-known that mastication of rubber directly influences the flow and vastly affects the viscosity of sols prepared from it (51). It is perhaps not so well-known that on mastication rubber at first becomes firmer and harder, and that this change soon gives way to an increasing softness, or that on allowing moderately worked rubber to stand it regains some of its firmness and elasticity (10).

It is also well-known that cold-worked metal often increases in stiffness, hardness, and brittleness, but it is not so generally understood that other properties also change. For instance, according to Austin and Pierce (2) the coefficient of expansion decreases as the result of cold-working.

In deforming crystals (26) the limit of elasticity can be raised several times by successive deformations. This strengthening in one direction is accompanied by weakening in another direction. Strengthened or weakened crystals after a time regain their normal condition.

Certain types of artificial stone are caused to set or harden by mechanical influences (29), and in clay articles we find differences between those made by casting and those made by extrusion.

Orientation in natural products has long been recognized. The wide occurrence of this phenomenon, as touched upon, for instance, by Bragg (5), seems to us to have a very special significance in surface phenomena. Hardy (18) early suggested that all molecules are more or less definitely oriented at interfaces, and this concept has been extended by Langmuir (27) for solutions.

Wilson (52) has proposed that pure liquids when drawn into thin films take on the properties of plastic solids, are stronger than the original liquid, may be stretched, and thus have elastic properties.
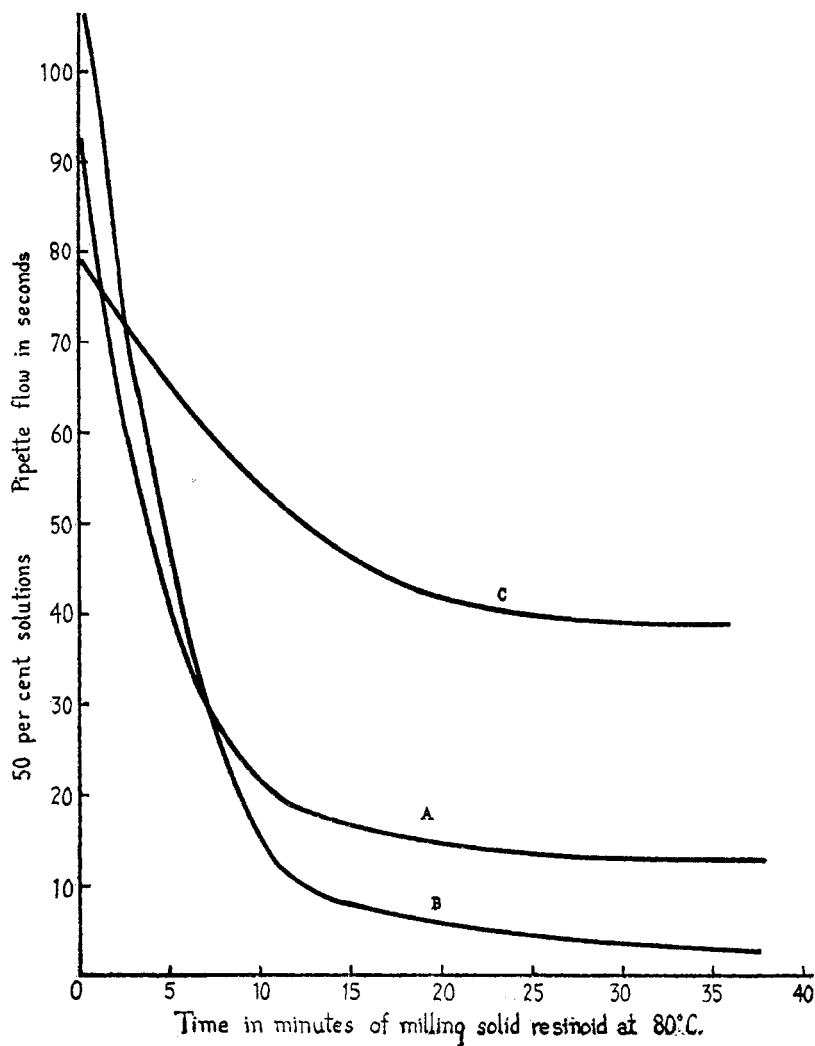

FIG. 3. EFFECT OF MILLING ON SOLID RESINOIDS

A, phenolic resinoid; B, alkyd resinoid; C, urea resinoid.   Measured in solvents

The colloid chemists have long agreed on the great strength of the surface layer as contrasted with the lesser strength of the mass of the same material (34).   It seems but a logical step to proceed from the consideration

of actual surfaces to consideration of films or surface skins of small but definite thickness.

If the effect of strengthening by flow is a true thin film effect as distinguished from a massive effect, one might find valuable data in the realm of films of molecular thickness. A recent publication (40) shows that thin film strengths may often increase with time, may reach high values, and may show remarkable elongation before breaking.

In "racked" rubber and in "fibrated" silk we appear to have film effects —either films in multiple layers or as threads—which may be considered as bundles of cylindrical films.

Clark (11) has given for stretched rubber a fairly complete picture closely agreeing with the above picture of stretched plastic silk. The two differ in one main detail, that is, the transformed plastic silk is permanent in form, as far as now known, whereas the racked rubber is permanent only below certain temperatures. For instance, if racked at 70°C. it is then permanent up to 40°C.

These "racking" and "fibration" or rearrangement effects in plastic substances have definite industrial value. This fact is becoming appreciated, as is shown by the current trend of research work. By orienting casein plastic a difference of strength of 600 per cent has been found in right angle directions. As the result of their studies, Manfred and Obrist (30) conclude that the flow of a casein plastic is lessened by the act of flow itself, whereas elasticity is increased by flow (31). Lately many patents have been issued on the stretching and working of spun rayon or cellulose derivatives. This operation gives increased strength (54), and involves a definite time factor for flow effects (55). The stretched fiber is far stronger to sudden load but is sensitive to increase of load per time unit, and under continued stress the strength fades to the same value as for unoriented rayon (22).

Sheppard and McNally (56) carried the flow effect into the film field, when for proper conditioning of the film they caused a film under tension to flow in a desired direction by means of pressure.

We now believe that many surface skin effects are caused by a type of reversible polymerization, as by rearrangement of micelles, and that such special surface films have different properties from the mass, that is, different average molecular weights, different solubilities, different strengths, densities, indices of refraction, etc.

The colloid concept of resinous micelles arranged in parallel layers, arrived at in one way by Staudinger and in another way by von Weimarn, will ultimately have a great influence on the study of resins. A recent diagrammatic representation of cellulose by Clark will be found of interest (12; also 41).

Staudinger found short isolated cylindrical bundles of fiber-like resinous masses, in form something like crystals but with amorphous properties. We note that slow long-time formation gave great micelle length, whereas short-time high temperature formation gave short lengths. This which we call skin effect looks like a directional influence analogous to the directional influences at work in crystal growth, but having perhaps a more profound effect on properties than is found in different crystal forms of the same substance. By intermittent longitudinal stretching and side compression von Weimarn was able to obtain progressively, from the surface inwardly, complete conversion of a mass of 0.02 mm. cross-section and of any convenient length, into a bundle of adhering threads.

Practical use of styrol resins came after control of resin quality by controlling the concentration of styrol in solution and its temperature of polymerization (49). An explanation of the varying degrees of toughness and brittleness is at hand in Staudinger's short and long micelles. Now a resin gel would seem to have a structural framework of long micelles with the physical nature and properties of the micelle influenced by temperature, by rate of formation, and by mechanical rearrangement.

This leads us to conceptions of resins as corresponding somewhat to that of cellulose. For instance, we can apply the cellulose concept of Meyer (35) that long primary valence chains unite to form a bundle (the micelle) through reciprocal lateral attraction. Also, Sponsler (44) interpreted the x-ray diagram of cellulose in terms of parallel oriented chains of unit groups held by primary valence.

Cellulose has properties which may some time greatly clarify the connection between structure and ultimate strength. Cotton fiber has tensile strength higher than that of copper (32). Regenerated cellulose is far less strong than the original cellulose, but it gains in strength when subjected to plastic flow such as stretching while in a swollen condition (23).

The natural cellulose structure, as in ramie cellulose, which consists of a series of concentric shells, shows great strength in one direction and much less strength at right angle thereto (45). Thermal expansion is ten times as great in one direction as in the right angle direction (19), and shrinkage is fifty to one hundred times as great transversely as longitudinally (6).

The cellulose fiber, for instance, cotton, is in the elongated or "fibrated" form of greatest strength, and any change is likely to be in the reverse direction, thus giving a resin-like and less strong massive form.

Mercerization or treatment with caustic soda solution causes the cotton fiber to shrink and weaken. It is therefore of great interest to find that caustic solutions have but little chemical effect below a certain concentration, but that such weak solutions have very great effect in causing contraction of the cotton thread (33). The contracted thread becomes

wiry and more brittle, that is more resin-like. The flexibility and strength of such thread may be partly restored by stretching the moist hot yarn. Mercerization of cotton increases iodine absorption, but when tension is used this iodine absorption is again reduced (21).

If in this resinous field needle-like amorphous micelles can form at the surface of plastic (supercooled melt) solids and can also form in solvents, then one should carefully consider cases where the melted plastic itself becomes the solvent. We have many cases of this in resins of abnormally high viscosity, high melting points, and abnormal solubility due, it would seem, to a polymeric structure within the mass. In the field of pure resinous masses one can find gels of every conceivable kind, reversible and irreversible, fusible and infusible, soluble and insoluble, hard and soft, etc.

According to Wright (53) alkyd resins are related in chemical and physical properties to drying oils. He says that gelation in both oils and alkyd resins depends upon escape of volatile products. In both cases degelling takes place if heated under pressure or in a confined space. Furthermore, while the alkyd resins may be plasticized to become an apparent physical match to celluloid, yet the celluloid mass may be molded and the alkyd resin structure will break down under the molding operation. Besides mechanical breakdown of the gel structure, the alkyd resin polymerization may be reversed by treatment with hot glycerol and also the resin may be vaporized, with decomposition, by application of dry heat above 250°C.

These polymerization phenomena are perhaps all reversible. For instance, hardened urea–formaldehyde resinoids dissolve easily in a 37 per cent water solution of formaldehyde, while phenolic resinoids dissolve with apparent depolymerization in phenolic solvents at about 300°C.

From this review of colloid literature we arrive at a common viewpoint of three fields, namely, rubbers, resins, and fibers; they seem to show some very close relationships. Rubber forms can be changed to resin forms and even to fiber forms. Resin forms can be changed to rubber forms and to fiber forms. Those products which are normally fibers may be changed to resins and to rubbers. Thus we are led to consider these molecules or micelles as mixtures of rods of varying size, kind, or condition, and to assign products to one or the other field depending upon rather general agreement in certain physical properties and irrespective of any definite agreement in chemical constitution.

With these similarities and differences in mind we may postulate a structural mechanism as a possible guide for further study of the connection between these three interlocking fields.

Having a mass with two or more rod forms present, let us assume no particular antagonism or attraction to exist between the different rods. Such a mass is an indiscriminate mixture with equal strengths in all direc-

tions. If, however, we push the pile, as into a thin plate, the motion will cause some rearrangement of the rods and increase in one direction the breaking strength of the oriented mass.

Now, if in a second case the rod ends are assumed to be points of mutual attraction, then as they slip past each other they should interact or interlock and we would have an endwise growth of micelles, or fiber-like forms. In case these new strong micelles resist chemical disruption, we would consider them as polymers. Rod forms of indifferent attractive forces would help to explain resins. Mutual attraction between rod forms would explain fibers and also explain some polymers, with all possible gradations in between.

Now having a mass with two or more rods present, let us assume a repulsive force between the ends of the rods. When such a mass is heated to a plastic flow range, the rods may be conceived to rearrange to greatest distance between ends, or at right angles to each other. Such a rearranged mass will resist and return from deformation, whether by stretching or by compression, and thus fall into the physical class of rubbers.

Rubber, resin, and fiber structures may thus be explained by the postulate that there are all possible variations of degree of attraction or of repulsion between rod forms of micelles. It should therefore be possible to pass temporarily from one state to another by simple motion, and, by assuming controlled variation in the degree of attraction, to explain those stable changes which range from minor to such major changes as transformation from one of these forms to either of the others.

The synthetic resin industry finds its major tasks in causing a controlled interruption, first, of chemical condensation, with simultaneous by-product elimination; second, of chemical polymerization, with the attendant change of particle size; and third, of physical polymerization, with corresponding change of properties due to enforced change of position. In the last two undertakings the principles of colloid chemistry find useful application.

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