"Urea-Formaldehyde Resins"

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Introduction:—

THE non-crystalline products formed by condensation of urea and formaldehyde, are usually referred to as urea-formaldehyde resins (or U-F resins), and belong to the well-known class of synthetic resins, wrongly, but generally called by the generic name of "Amino resins" or "Aminoplasts." Strictly speaking, U-F resins should be classed as amido resins, but because of similarity of performance of urea resins and melamine resins, the term "Amino resins" is employed to include both the amine and the amide condensation products with formaldehyde. Instead of urea, thiourea or guanidine, which are analogous to urea in structure, as also dicyandiamide and melamine can be used to give resins with properties comparable to those of U-F resins. However, because of the low price and ease of manufacture, coupled with good durability, pale colour and fastness to light, U-F resins are finding by far the largest number of uses and applications.

U-F resins can be looked upon as truly synthetic resins, as the basic raw materials, urea and formaldehyde, can be manufactured from simple materials like carbon dioxide, nitrogen and hydrogen. However, unlike synthetic resins, such as phenol-formaldehyde condensates, polystyrene, polymethyl methacrylate, etc., U-F resins by themselves possess little or no useful properties and have to be employed with other ingredients in order to bring out their many desirable characteristics. Thus, U-F resins are employed with cellulosic fillers to give moulding powders, or applied to cellulosic fabrics to impart such properties as crease-resistance and stiffness; they can also be used as adhesives for wood, and for increasing the wet-strength of paper. Modified with an appropriate alcohol, they find use in various types of surface coatings. The production of U-F resins, therefore, has acquired considerable importance in the industrially advanced countries and despite competition from various natural and synthetic products they continue to hold their own.

History:—

The reaction between urea and formaldehyde was studied by Holzer, Goldschmidt, John and others, but the first systematic work on the resinous products appears to have been carried out by Einhorn and Hamburger. Goldschmidt and Neuss, Mittasch and Raustetter also studied the condensation reaction of urea and formaldehyde employing mineral acids, acid salts and organic acids as condensing agents. The industrial development of U-F resins, however, was due to Pollak, who was the first to prepare moulding powders which could be fabricated by techniques similar to those employed for processing of phenol-formaldehyde powders. Pollak was the first to realise the importance of carrying out the reaction in two stages to get useful products, with superior performance. Urea is first condensed with formaldehyde under alkaline conditions and the intermediate products so obtained are blended with cellulosic fillers and subsequently cured under acid conditions to give the moulded articles. It may be added that his attempts to prepare an "organic glass" from the intermediate U-F condensate were not successful. The production of moulding powders was then taken up by British

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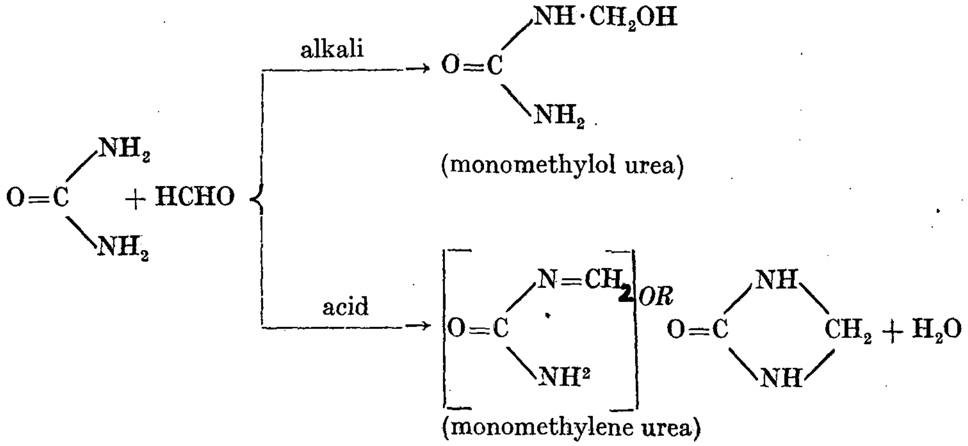
Cyanides Ltd., who also started manufacturing moulding powders based on thiourea. Much of the information regarding moulding powders is to be found only in patent literature, particularly as regards the catalyst to be employed to get the final cure.

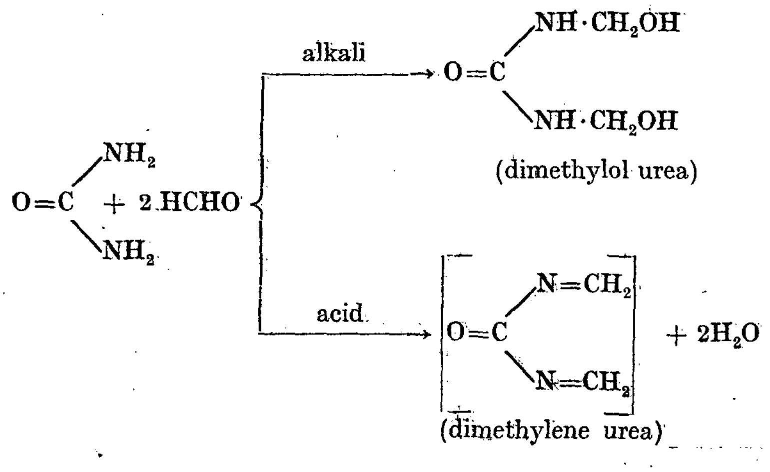
In 1926, Tootal Broadhurst Lee Co., Ltd., patented a process employing the condensation product of urea and formaldehyde for rendering cellulosic fibers and fabrics, shrink or crease resistant. Adhesives suitable for bonding of wood were developed in Germany in 1936 while the modification of U-F resin condensates by means of monohydric alcohols to obtain products useful in surface coatings was first described by Hodgins and Hovey.

Since many of the earlier patents on U-F resins have now expired, there is at present a considerable interest in the use of these materials and a number of newer and better uses have been developed in recent years.

Chemistry of U-F Resins: —

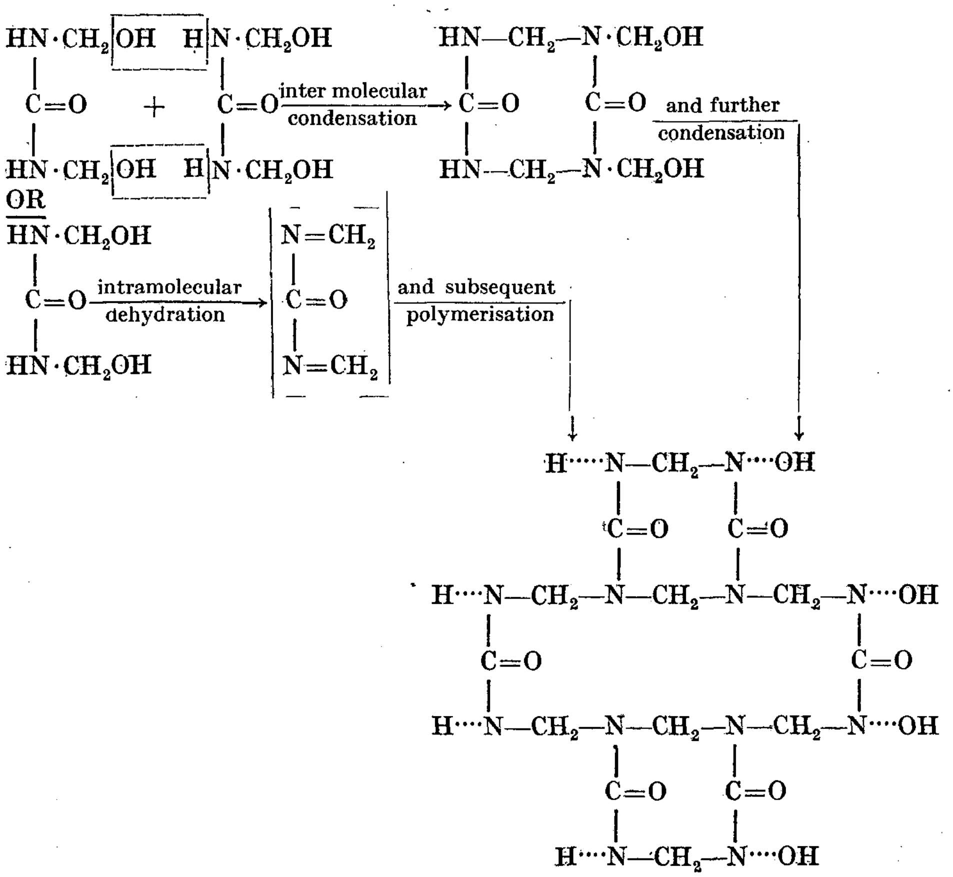
The primary reactions which occur when urea is condensed with formaldehyde in aqueous solution, are the formation of methylol derivatives under alkaline conditions, and methylene derivatives under acid conditions.





While the methylol derivatives have been obtained as crystalline products, the methylene derivatives have not been isolated, as only resinous compounds are obtained under acid conditions. However, certain polymeric substances with a definite structure have been claimed to have been isolated by working in glacial acetic acid medium.

The reactions that occur when the methylol derivatives subsequently condense are, however, not completely understood. As water is liberated during the condensation, one can presume that either of the following reactions have occurred:—



Cross-linked 3-dimensional structure of U-F resin.

In the first case, the hydroxyl group of the methylol urea reacts with H of the HN— group of another molecule of dimethylol urea with the elimination of water; in the second case, intramolecular dehydration occurs with the formation of the hypothetical dimethylene urea which subsequently polymerises in a manner similar to vinyl compounds. In either case, the final products will have similar structures. As the fully cured resin is insoluble and infusible, there is no unambiguous proof for its structure. It is, however, generally accepted that the resin will be essentially composed of 8-membered ring systems without end methylol groups, the end valencies being satisfied by H and OH groups. The only evidence in favour of the above hypothesis is the nitrogen content of the fully cured resin which is in close agreement with that determined experimentally.

An alternate structure for the fully cured resin suggested by Redfarn

$$\begin{array}{ccc} \mathrm{CH_2} & & \mathrm{CH_2} \\ \| & & \| \\ \mathrm{N} & \mathrm{-CO-} & \mathrm{N} \end{array} \longrightarrow \begin{array}{ccccccccccc} \cdots\mathrm{CH_2} & & \mathrm{CH_2} & - & \mathrm{CH_2} & & \mathrm{CH_2} & - & \mathrm{CH_2} & & \mathrm{CH_2}\cdots \\ | & & | & & | & & | & & | & & | \\ \cdots\mathrm{N} & \mathrm{-CO-} & \mathrm{N} & - & \mathrm{N} & \mathrm{-CO-} & \mathrm{N} & - & \mathrm{N} & \mathrm{-CO-} & \mathrm{N}\cdots \end{array}$$

is unlikely to be correct, as the properties of the fully cured material are not at all characteristic of linear molecules.

The structure of U-F resin is of comparatively minor importance, for the *resin by itself has no useful application.* The optimum properties of U-F resin intermediates are developed only in conjunction with other molecules containing hydroxyl or similar reactive groups. Thus, just as methylol ureas can give ethers with butyl or amyl alcohol, the methylol derivatives combine with the hydroxyl groups of the added material to give complex ethers. In moulding powders, the cellulosic filler supplies the necessary hydroxyl group, while in organic surface coatings "the plasticising resin" (castor oil modified glycerol phthalate resin, monoglycerides, blown castor oil, etc.) does the needful. The adhesion of U-F resin to wood and the very high strength of the bond so obtained is also readily explained on the same basis. In textile finishes the U-F resin actually goes in combination with the fibre molecules and because primary valence linkages are formed, the incidental effects of stiffness, lower water absorption, etc., are developed.

Dimethylol urea formed by condensing 1 mole of urea with 2 moles of formaldehyde is, however, not necessary for the production of industrial U-F resins, where a lower formaldehyde ratio is desirable as the resin intermediate has to combine with the reactive groups of the filler or plasticiser. For the production of U-F moulding powders, a ratio of 1 mole urea to 1.5 moles formaldehyde has become the general practice since it has been found that a lower formaldehyde ratio gives a more rapidly thermosetting product, with reduced gassing—*i.e.*, *less liberation of vapours* during the moulding process, and a finished product with decreased water absorption. Similarly, specific ratios have to be employed, when the final product is to be used in surface coatings, adhesives or textile finishes. However, in order to prolong the shelf life of the resin syrups, higher formaldehyde ratios are sometimes employed.

The type of intermediate formed as also the rate and extent to which the reaction proceeds is dependent not only on molecular ratio of the reactants, but also on factors like concentration, time and temperature, pH of the solution and the type of catalyst. Exhaustive study of the kinetics of U-F reactions has been described by G. Smets and A. Borzee.[1]

Uses of U-F Resins:—

(1) *Moulding Powders*: Details regarding the manufacture of U-F resin syrups are not available in published literature but it is understood that the syrup is prepared by reacting 1 mole urea with 1.5 moles formaldehyde (as formalin) under alkaline conditions. The amount and type of alkali used, as also the temperature at which reaction is carried out, are closely guarded trade secrets. The syrup should be in a low

state of condensation and sufficiently hydrophilic in order to incorporate the filler uniformly with a minimum amount of power consumption. As urea resins are noted for their pale colour, the syrup is generally prepared in glass-lined resin kettles, though nickel alloys or even aluminium have been claimed to be satisfactory. The syrup may be concentrated by vacuum distillation prior to incorporating the filler. The blending is generally carried out at about 50°C in heavy duty mixers provided with appropriate type of mixing gear. *Alpha*-cellulose or chemical cotton, as also bleached sulphite pulp is the preferred filler, though, when the colour of final products is of minor importance, other cellulosic fillers like wood flour or walnut shell powder can also be employed. The wet pulpy mixture is dried in trays at temperatures below 90°C. At this stage, the material still contains a certain amount of combined moisture (about 7%). It is, however, essential to have a small quantity of moisture as otherwise the moulding powder will not have the required degree of flow. The dried powder is then disintegrated and blended with other additives in a ball mill. Mould lubricants like stearic acid or stearates and a hardening agent which is usually an acid or latent acid, are the most essential of these additives; pigments, colourants, etc., may be added to meet specific requirements.

An alternative process, referred to as the "dry process" may also be employed. In this case, the U-F condensate is obtained as a free flowing powder by dehydrating under vacuum or by spray drying. The powder is then blended with the filler and the mixture is subsequently compounded on hot-roll mills into thin sheets. The latter, on cooling, is brittle enough to be disintegrated to a fine powder which is subsequently mixed with lubricants, accelerators, etc., in the usual manner.

U-F resins are generally fabricated by compression moulding or its modification, transfer moulding. It is not suitable for injection moulding or extrusion. The moulding is generally carried out at temperatures between 130-150°C, pressures ranging from 1 to 3 tons/sq. inch. The material of construction of the mould, however, should be acid resistant, and as such, in certain cases, even gold-plated moulds have been claimed to be employed.

The moulded articles possess a number of excellent characteristics. They are resistant to oxidation, to oil, grease, weak alkalies, weak acids, alcohol and other solvents. They are very hard, resist abrasion and scratching. As they have no taste and smell, they are popular for the production of domestic ware. Urea resins possess excellent insulating characteristics. Probably, the best known mouldings made with U-F resins are tableware—cups, saucers, plates, trays, lampshades, reflectors, etc.

(2) *Surface Coatings*: U-F resins as such, are unsuitable for use in surface coatings, as the films formed are brittle and lack adhesion. It is, therefore, essential to use them in conjunction with the appropriate plasticiser. In order that U-F resins are rendered compatible with plasticisers, it is necessary to modify the U-F resin intermediates with a suitable alcohol. Modified U-F resins in conjunction with the appropriate plasticiser are best employed in pigmented finishes of the baking type, though air-drying compositions are also known.

A number of methods for the manufacture of U-F varnish resins are known, but the most widely employed method is condensation of urea, formaldehyde and butyl alcohol in the presence of an acid catalyst and removal of the free water and water of reaction by azeotropic distillation. The resin is usually made available as a 50-60% solution in butyl alcohol. In recent years, resins soluble in hydrocarbon solvents have been marketed in solid form. The resin of this type can be dissolved in any appropriate organic solvent to give a solution which can be used in preparation of stoving enamels.

The U-F-alkanol resins are best employed in pigmented coatings after being plasticised with appropriate material (the best is oil-modified alkyd resin), the choice of which is governed by the properties desired in the end products. U-F resins have acquired great importance as baking enamels. This type of enamel is employed for many widely used products such as refrigerators, hospital equipment, hardware, industrial equipment and indeed all articles which are able to stand the baking temperatures.

(3) *Adhesives*: The manufacture of adhesives may be regarded as the most important application of U-F resins. The adhesives can be used either by cold- or hot-pressing methods; they are resistant to moisture, unaffected by bacteria, fungi, high temperature and corrosive action and are widely used for plywood manufacture, air-craft construction, boat building, house construction, etc. The adhesives are always used in conjunction with a " hardener," which is mixed with the resin syrup just prior to use. It could also be applied to one surface to be joined, the adhesive being applied to the other surface. The function of the hardener is to bring about a chemical and physical change in the adhesive, leading first to its gelatinisation and finally to setting. The hardener is usually a weak acid. The stronger the acid, the more rapid will be the setting action. The ability to extend or load these resin adhesives with rye flour or starch has an important bearing on the cost. The water resistance of such joints is not so high as that of those made with the pure adhesive, but is better than those obtained with many other adhesives.

The liquid resins are generally prepared by condensing urea and formaldehyde under slightly acid conditions to a predetermined degree. The resin solution is then neutralised and water removed by distillation under reduced pressure until the required viscosity or solid content is achieved. The addition of certain metal salts prior to the condensation is said to give resins with increased stability. Zinc chloride, alkaline earth chlorides such as calcium chloride, may be employed for this purpose.

Urea resins to be used as adhesives are now available in the form of powders. The dry powder may be kept for over a year provided that it is kept cool, and it only requires to be mixed with the appropriate quantity of cold water to regenerate a liquid adhesive having all the desirable properties of the resin syrup which is used with hardeners as before.

Recently, urea adhesive " foams " have been developed for use in the manufacture of thin sheets of plywood.

(4) *Textile Finishes*: The use of U-F resins in textile finishes is on the decrease because of the superiority and ease of cure obtainable with melamine-formaldehyde resins. However, because the original patents have expired, there is a renewed interest.

Urea resin solutions for use in textile finishes are generally prepared by the consumer himself, though stabilised U-F resin syrups in water are also available. A ratio of 1 mole of urea to 1.6 moles of formaldehyde is generally preferred and the initial condensation is carried out in the presence of weak alkali usually ammonia. The condensation is carried out further in the presence of a hydroxy acid and the syrups so obtained are subsequently employed in textile finishes. The treated fabric, however, has to be heated at temperatures between 120—130°C to bring about the necessary combination between the resin and cellulose. The stoved fabric is then soaped, washed and dried. For obtaining satisfactory crease resistance, at least 8-14% resin must be present on the fabric.

U-F resins have also been employed in textile printing in the form of pigmented lacquer-resin emulsions.

Miscellaneous applications: U-F resins have been employed in the production of wet strength paper. Wet strength paper is paper that has been specifically treated so that it retains a considerable proportion of its dry tensile and bursting strengths when completely saturated with water. Urea resins, as also melamine resins are capable of conferring wet strength to paper when applied in small quantities. The resins employed are similar to those used for adhesives and textile finishes.

U-F resins have been used in the bonding of sand grains to make the cores and moulds used in the casting of metals. It is found that where rapid breakdown of binder and easy knockout are required, U-F resins have advantages over other foundry sand-binders. U-F resin cores of high dry strength can safely be used for light-alloy castings, thus greatly reducing core breakage and improving casting finish.

Another contribution of U-F resins is in the field of orthopædic surgery.[2] Although, plaster of paris is used extensively, it is known to suffer from a number of defects, including impermeability to X-rays, lack of resistance to water and an inherent brittleness. It is possible by the use of U-F resin adhesives, used alone or in conjunction with other additives, to overcome some of these defects. The techniques developed so far are far from perfect, and much remains to be done to make it a worthwhile contribution to orthopædic surgery.

U-F resins are also used in the form of foamed resins and in solid-dot Braille printing. Aqueous solutions of U-F condensates are used as laminating agents in much the same manner as phenolic resins. Uses of U-F resins in conjunction with deodourising and preserving agents for the preservation of perishable animal products such as hides, impregnation of leather, to fix the residual tanning substances, are also known. Urea and other fertilisers which are hygroscopic or have a tendency to cake during storage, can be preserved by coating with a U-F condensate. The most recent use of U-F resin is as a blasting explosive[3] for which a patent has been taken.

Production of U-F Resins in India:—

The wide variety of applications of U-F resins in different industries is sufficient proof for starting the production of this synthetic resin in India. The first question one would ask: "Are the raw materials available ? What are the prospects for their production ? Would the resins have a ready market?"

There is every likelihood of urea and formaldehyde being manufactured in the near future. It is understood that there are plans to install a urea plant near the Government Fertiliser Factory at Sindri (Bihar)[4] capable of producing 10,000 tons per annum. This plant, when established, will be able to divert a portion of its production for use in the plastics industry. Formaldehyde was being manufactured on a small scale at Bhadravati (Mysore) from methyl alcohol obtained as a by-product in the destructive distillation of wood. A plant for the manufacture of synthetic methyl alcohol is also being planned at Sindri. As *al-*

pha-cellulose of good quality is available, a small unit for the manufacture of urea resins with a capacity of 400 tons of resins per annum and equipped for the production of 500-600 tons of moulding powder per annum could successfully satisfy the immediate requirements of the different industries consuming this resin. The plant and equipment required are simple and could readily be fabricated in this country.

As for their use in surface coatings, much will depend on the availability of butyl alcohol, though, fractionated fusel oil, a by-product of the alcohol industry, may perhaps be employed. There is an established market for U-F adhesives in the manufacture of plywood and there is considerable interest in the use of U-F resins for finishing of rayon textiles. Thus, the market for the products is assured and if the raw materials are available, the prospects for establishing a U-F resin industry appear to be attractive.

BIBLIOGRAPHY :

1. Ellis, C.—" Chemistry of Synthetic Resins "—Vol. 1, Reinhold Publishing Corp., New York, 1935.
2. Barron, H.—" Modern Plastics "—1st Edition, Chapman and Hall Ltd., London, 1946.
3. Vale, C. P.—" Aminoplastics "—1st Edition, Cleaver-Hume Press Ltd., London, 1950.
4. Delmonte, J.—" Technology of Adhesives "—1st Edition, Reinhold Publishing Corp., New York, 1947.
5. Morrel and Langton—" Synthetic Resins and Allied Plastics "—3rd Edition, Oxford University Press, London, 1951.
6. Plastics Progress—" Papers and Discussions at the British Plastics Convention, 1951 "—Iliffe and Sons Ltd., London, 1951.
7. Modern Plastics Encyclopædia—Plastics Catalogue Corp., New York, 1953.

REFERENCES :

1. Smets, G. and Borzee, A., **Journal of Polymer Science**, 1952, 4, 371.
2. Collinson, H., **British Plastics**, 1946, 18, 253.
3. **Chemical Trade Journal and Chemical Engineer**, 1954, 135, 120.
4. Survey of Research Problems in Plastics with special reference to the development of Plastics Industry in India, C.S.I.R. Report, 1954, p. 44, New Delhi.