AMINO RESINS AND PLASTICS

1. Introduction

Amino resins are thermosetting polymers made by combining analdehyde with a compound containing anamino (—NH_2) group. Urea–formaldehyde (U/F) accounts for >80% of amino resins; melamine–formaldehyde accounts for most of the rest. Other aldehydes and other amino compounds are used to a very minor extent. The first commercially important amino resin appeared ~1930, or some 20 years after the introduction of phenol–formaldehyde resins and plastics (see PHENOLIC RESINS).

The principal attractions of amino resins and plastics are water solubility before curing, which allows easy application to and with many other materials, colorlessness, which allows unlimited colorability with dyes and pigments, excellent solvent resistance in the cured state, outstanding hardness and abrasion resistance, and good heat resistance. Limitations of these materials include release of formaldehyde during cure and, in some cases, such as in foamed

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insulation, after cure, and poor outdoor weatherability for urea moldings. Repeated cycling of wet and dry conditions causes surface cracks. Melamine moldings have relatively good outdoor weatherability.

Amino resins are manufactured throughout the industrialized world to provide a wide variety of useful products. Adhesives (qv), representing the largest single market, are used to make plywood, chipboard, and sawdust board. Other types are used to make laminated wood beams, parquet flooring, and for furniture assembly (see WOOD-BASED COMPOSITES AND LAMINATES).

Some amino resins are used as additives to modify the properties of other materials. For example, a small amount of amino resin added to textile fabric imparts the familiar wash-and-wear qualities to shirts and dresses. Automobile tires are strengthened by amino resins that improve the adhesion of rubber totire cord (qv). A racing sailboat may have a better chance to win because the sails of Dacron polyester have been treated with an amino resin (1). Amino resins can improve the strength of paper even when it is wet. Molding compounds based on amino resins are used for parts of electrical devices, bottle and jar caps, molded plastic dinnerware, and buttons.

Amino resins are also often used for the cure of other resins such as alkyds and reactive acrylic polymers. These polymer systems may contain 5–50% of the amino resin and are commonly used in the flexible backings found on carpets and draperies, as well as in protective surface coatings, particularly the durable baked enamels of appliances, automobiles, etc.

The term amino resin is usually applied to the broad class of materials regardless of application, whereas the term aminoplast or sometimes amino plastic is more commonly applied to thermosetting molding compounds based on amino resins. Amino plastics and resins have been in use since the 1920s. Compared to other segments of the plastics industry, they are mature products, and their growth rate is only about one-half of that of the plastics industry as a whole. They account for ~3% of the U.S. plastics and resins production.

1.1. History. The basic chemistry of amino resins was established as early as 1908 (2), but the first commercial product, a molding compound, was patented in England (3) only in 1925. It was based on a resin made from an equimolar mixture of urea and thiourea and reinforced with purified cellulose fiber and was trademarked Beetle (indicating it could "beat all" others). Patent rights were acquired by the American Cyanamid Company along with the Beetle trademark. By 1930 a similar molding compound was being marketed in the United States. The new product was hard and not easily stained and was available in light, translucent colors; furthermore, it had no objectionable phenolic odor. The use of thiourea improved gloss and water resistance, but stained the steel molds. As amino resin technology progressed the amount of thiourea in the formulation could be reduced and finally eliminated altogether.

In the early 1920s, experimentation withurea–formaldehyde resins [9011-05-6] in Germany (4) and Austria (5,6) led to the discovery that these resins might be cast into beautiful clear transparent sheets, and it was proposed that this new synthetic material might serve as an organic glass (5,6). In fact, an experimental product called Pollopas was introduced, but lack of sufficient water resistance prevented commercialization. Melamine–formaldehyde resin [9003-08-1] does have better water resistance but the market for synthetic glass was taken over by new thermoplastic materials such as polystyrene and poly(methyl methacrylate) (see METHACRYLIC POLYMERS; STYRENE PLASTICS).

Melamine resins were introduced about ten years after the Beetle molding compound. They were very similar to those based on urea but had superior qualities. In Germany, Henkel was issued a patent for a melamine resin in 1936 (7). Melamine resins rapidly supplanted urea resins and were soon used in molding, laminating, and bonding formulations, as well as for textile and paper treatments. The remarkable stability of the symmetrical triazine ring made these products resistant to chemical change once the resin had been cured to the insoluble, cross-linked state.

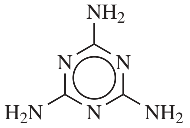
Prior to the rapid expansion of thermoplastics following World War II, amino plastics served a broad range of applications in molding, laminating, and bonding. As the newer and more versatile thermoplastic materials moved into these markets, aminos became more and more restricted to applications demanding some specific property best offered by the thermosetting amino resins. Current sales patterns are very specific. Urea molding powders find application in moldings for electrical devices and in closures for jars and bottles. Melamine molding compound is used principally for molded plastic dinnerware. Urea resins have retained their use in electrical wiring devices because of good electrical properties, good heat resistance, and an availability of colors not obtainable with phenolics. Urea–formaldehyde resins are useful as closures because of their excellent resistance to oils, fats, and waxes often found in cosmetics, and their availability in a broad range of colors. Melamine plastic is used for molded dinnerware primarily because of outstanding hardness, water resistance, and stain resistance. Melamine–formaldehyde is the hardest commercial plastic material.

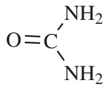
Aminoplasts and other thermosetting plastics are molded by an automatic injection molding process similar to that used for thermoplastics, but with an important difference (8). Instead of being plasticized in a hot cylinder and then injected into a much cooler mold cavity, the thermosets are plasticized in a warm cylinder and then injected into a hot mold cavity where the chemical reaction of cure sets the resin to the solid state. The process is best applied to relatively small moldings. Melamine plastic dinnerware is still molded by standard compression-molding techniques. The great advantage of injection molding is that it reduces costs by eliminating manual labor, thereby placing the amino resins in a better position to compete with thermoplastics (see PLASTICS PROCESSING).

The future for amino resins and plastics seems secure because they can provide qualities that are not easily obtained in other ways. New developments will probably be in the areas of more highly specialized materials for treating textiles, paper, etc, and for use with other resins in the formulation of surface coatings, where a small amount of an amino resin can significantly increase the value of a more basic material. Additionally, since amino resins contain a large proportion of nitrogen, a widely abundant element, they may be in a better position to compete with other plastics as raw materials based on carbon compounds become more costly.

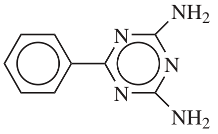
2. Raw Materials

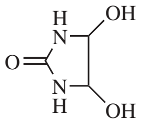
Most amino resins are based on the reaction offormaldehyde [50-00-0] with urea [57-13-6] or melamine [108-78-1]

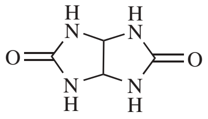

melamine


urea

Although formaldehyde will combine with many other amines, amides, and aminotriazines to form useful products, only a few are used and are of minor importance compared to products based on urea and melamine. Benzoguanamine [91-76-9], eg, is used in amino resins for coatings because it provides excellent resistance to laundry detergent, a definite advantage in coatings for automatic washing machines. Dihydroxyethylene urea [3720-97-6] is used for making amino resins that provide wash-and-wear properties in clothing. Glycoluril [496-46-8] resins provide coatings with high film flexibility.


benzoguanamine


dihydroxyethyleneurea


glycoluril

Aniline–formaldehyde resins were once quite important because of their excellent electrical properties, but their markets have been taken over by newer thermoplastic materials. Nevertheless, some aniline resins are still used as modifiers for other resins. Acrylamide (qv) occupies a unique position in the amino resins field since it not only contains a formaldehyde reactive site, but also a polymerizable double bond. Thus it forms a bridge between the formaldehyde condensation polymers and the versatile vinyl polymers and copolymers.

In the sense that formaldehyde can supply a methylene link between two molecules, it is difunctional. Each amino group has two replaceable hydrogens that can react with formaldehyde; hence, it also is difunctional. Since the amino compounds commonly used for making amino resins, urea, and melamine contain two and three amino groups, they are polyfunctional and react with formaldehyde to form three-dimensional, cross-linked polymer structures. Compounds with a single amino group such as aniline or toluenesulfonamide can usually react with formaldehyde to form only linear polymer chains. However, in the presence of an acid catalyst at higher temperatures, the aromatic ring of aniline may react with formaldehyde to produce a cross-linked polymer.

2.1. Urea. Urea (carbamide) CH_4N_2O, is the most important building block for amino resins because urea–formaldehyde is the largest selling amino resin, and urea is the raw material for melamine, the amino compound used in the next largest selling type of amino resin. Urea is also used to make a variety of other amino compounds, such as ethyleneurea, and other cyclic derivatives used for amino resins for treating textiles. They are discussed later.

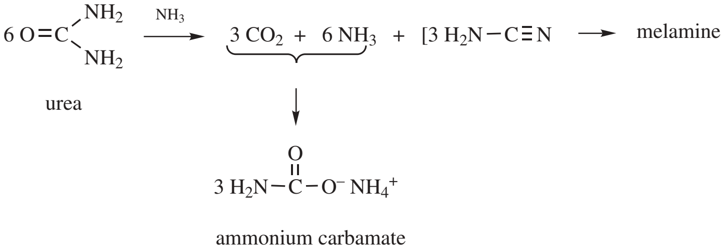
Urea is soluble in water, and the crystalline solid is somewhat hygroscopic, tending to cake when exposed to a humid atmosphere. For this reason, urea is frequently pelletized or prilled (formed into little beads) to avoid caking and making it easy to handle.

Only ∼10% of the total urea production is used for amino resins, which thus appear to have a secure source of low cost raw material. Urea is made by the reaction of carbon dioxide and ammonia at high temperature and pressure to yield a mixture of urea and ammonium carbamate; the latter is recycled.

$$CO_2 + 2\,NH_3 \longrightarrow NH_2CONH_2 + H_2O \rightleftharpoons H_2NCOONH_4$$

2.2. Melamine. Melamine (cyanurotriamide,2,4,6-triamino-*s*-triazine) $C_3H_6N_6$, is a white crystalline solid, melting at approximately 350°C with vaporization, only slightly soluble in water. The commercial product, recrystallized grade, is at least 99% pure. Melamine was synthesized early in the development of organic chemistry, but it remained of theoretical interest until it was found to be a useful constituent of amino resins. Melamine was first made commercially from dicyandiamide [461-58-5] (see CYANAMIDES), but is now made from urea, a much cheaper starting material (9–12) (see also CYANURIC AND ISOCYANURIC ACIDS).

Urea is dehydrated to cyanamide which trimerizes to melamine in an atmosphere of ammonia to suppress the formation of deamination products. The ammonium carbamate [1111-78-0] also formed is recycled and converted to urea. For this reason the manufacture of melamine is usually integrated with much larger facilities making ammonia and urea.



Since melamine resins are derived from urea, they are more costly and are therefore restricted to applications requiring superior performance. Essentially all of the melamine produced is used for making amino resins and plastics.

2.3. Formaldehyde. Pure formaldehyde, CH_2O, is a colorless, pungent smelling reactive gas (see FORMALDEHYDE). The commercial product is handled either as solid polymer, paraformaldehyde (13), or in aqueous or alcoholic solutions. Marketed under the trade name Formcel, solutions in methanol, *n*-butanol, and isobutyl alcohol, made by Hoechst-Celanese, are widely used for making alcohol-modified urea and melamine resins for surface coatings and treating textiles.

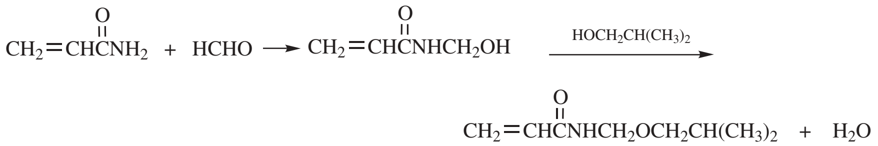
Aqueous formaldehyde, known as formalin, is usually 37 wt % formaldehyde, though more concentrated solutions are available. Formalin is the general-purpose formaldehyde of commerce supplied unstabilized or methanol stabilized. The latter may be stored at room temperature without precipitation of solid formaldehyde polymers because it contains 5–10% methanol. The uninhibited type must be maintained at a temperature of at least 32°C to prevent the separation of solid formaldehyde polymers. Large quantities are often supplied in more concentrated solutions. Formalin at 44, 50, or even 56% may be used to reduce shipping costs and improve manufacturing efficiency. Heated storage tanks must be used. For example, formalin containing 50% formaldehyde must be kept at a temperature of 55°C to avoid precipitation. Formaldehyde solutions stabilized with urea (U) are used (14), and various other stabilizers have been proposed (15,16). With urea-stabilized formaldehyde (F) the user need only adjust the U/F ratio by adding more urea to produce a urea resin solution ready for use.

Paraformaldehyde [30525-89-4] is a mixture of polyoxymethylene glycols, $HO(CH_2O)_nH$, where n is from 8 to as much as 100. It is commercially available as a powder (95%) and as flake (91%). The remainder is a mixture of water and methanol. Paraformaldehyde is an unstable polymer that easily regenerates formaldehyde in solution. Under alkaline conditions, the chains depolymerize from the ends, whereas in acid solution the chains are randomly cleaved (17). Paraformaldehyde is often used when the presence of a large amount of water should be avoided as in the preparation of alkylated amino resins for coatings. Formaldehyde may also exist in the form of the cyclic trimer trioxane [110-88-3]. This compound is fairly stable and does not easily release formaldehyde, hence it is not used as a source of formaldehyde for making amino resins.

Approximately 25% of the formaldehyde produced in the United States is used in the manufacture of amino resins and plastics.

2.4. Other Materials. Benzoguanamine and acetoguanamine may be used in place of melamine to achieve greater solubility in organic solvents and greater chemical resistance. Aniline and toluenesulfonamide react with formaldehyde to form thermoplastic resins. They are not used alone, but rather as plasticizers (qv) for other resins including melamine and urea–formaldehyde. The plasticizer may be made separately or formed *in situ* during preparation of the primary resin.

Acrylamide [79-06-1] is an interesting monomer for use with amino resins; the vinyl group is active in free-radical catalyzed addition polymerizations, whereas the $-NH_2$ group is active in condensations with formaldehyde. Many patents describe methods of making cross-linked polymers with acrylamide by taking advantage of both vinyl polymerization and condensation with formaldehyde. For example, acrylamide reacts readily with formaldehyde to form N-methylolacrylamide [924-42-5], which gives the corresponding isobutyl ether with isobutyl alcohol.



$$CH_2{=}CH\overset{O}{\overset{\|}{C}}NH_2 + HCHO \longrightarrow CH_2{=}CH\overset{O}{\overset{\|}{C}}NHCH_2OH \xrightarrow{HOCH_2CH(CH_3)_2} CH_2{=}CH\overset{O}{\overset{\|}{C}}NHCH_2OCH_2CH(CH_3)_2 + H_2O$$

This compound is soluble in most organic solvents and may be easily copolymerized with other vinyl monomers to introduce reactive side groups on the polymer chain (18). Such reactive polymer chains may then be used to modify other polymers including other amino resins. It may be desirable to produce the cross-links first. Thus, *N*-methylolacrylamide can react with more acrylamide to produce methylenebisacrylamide, a tetrafunctional vinyl monomer.

$$CH_2{=}CH\overset{O}{\overset{\|}{C}}NHCH_2OH + CH_2{=}CH\overset{O}{\overset{\|}{C}}NH_2 \longrightarrow CH_2{=}CH\overset{O}{\overset{\|}{C}}NHCH_2NHCCH{=}CH_2 + H_2O$$

3. Chemistry of Resin Formation

The first step in the formation of resins and plastics from formaldehyde and amino compounds is the addition of formaldehyde to introduce the hydroxymethyl group, known as methylolation or hydroxymethylation.

$$R{-}NH_2 + HCHO \longrightarrow R{-}NH{-}CH_2OH$$

The second step is a condensation reaction that involves the linking together of monomer units with the liberation of water to form a dimer, a polymer chain, or a vast network. This reaction is usually referred to as methylene bridge formation, polymerization, resinification, or simply cure, and is illustrated in the following equation:

$$RNH{-}CH_2OH + H_2NR \longrightarrow RNH{-}CH_2{-}NHR + H_2O$$

Success in making and using amino resins largely depends on the precise control of these two chemical reactions. Consequently, these reactions have been much studied (19–30).

The first reaction, the addition of formaldehyde to the amino compound, is catalyzed by either acids or bases. Hence, it takes place over the entire pH range. The second reaction joins the amino units with methylene links and is catalyzed only by acids. The rates of these reactions have been studied over a broad range of pH (28). The results are presented in Figure 1.

The same study also examined some of the subsequent reactions involved in the formation of more complex U/F condensation products. Rate constants for these reactions at 35°C are shown in Table 1.

The methylol compounds produced by these reactions are relatively stable under neutral or alkaline conditions, but undergo condensation, forming polymeric products under acid conditions. Consequently, the first step in making an amino plastic is usually carried out under alkaline conditions. The amino compound and formaldehyde are combined and form a stable resin intermediate that may be used as an adhesive or combined with filler to make a molding compound. The second step is the addition of an acidic substance to catalyze the curing reaction, often with the application of heat to cure the amino resin to the solid cross-linked state. In this reaction, the methylol group is probably protonated and a molecule of water lost, giving the intermediate carbonium–imonium ion, which then reacts with an amino group to form a

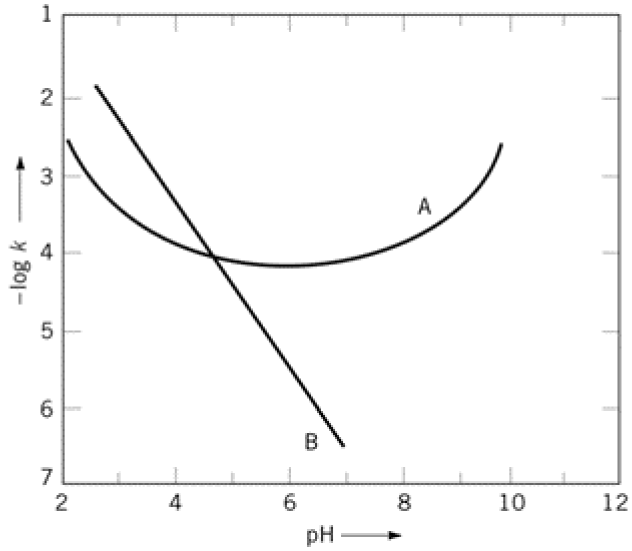


Fig. 1. Influence of pH on A, the addition reaction of urea and formaldehyde (1:1); and B, the condensation of methylolurea with the amino hydrogen of a neighboring urea molecule. Temperature = 35°C; 0.1 *M* aq.

methylene link.

$$\mathrm{RNHCH_2OH + H^+ \rightleftharpoons RNHCH_2\overset{+}{O}H_2}$$

$$\mathrm{RNHCH_2\overset{+}{O}H_2 \rightleftharpoons RNH\overset{+}{C}H_2 + H_2O}$$

$$\mathrm{RNH\overset{+}{C}H_2 + H_2NR' \rightleftharpoons RNHCH_2H_2\overset{+}{N}R'}$$

$$\mathrm{RNHCH_2H_2\overset{+}{N}R' \rightleftharpoons RNHCH_2HNR' + H^+}$$

In addition to the two main reactions, ie, methylolation and condensation, there are a number of other reactions important for the manufacture and uses of amino resins. For example, two methylol groups may combine to produce a dimethylene ether linkage and liberate a molecule of water:

$$2\,\mathrm{RNHCH_2OH} \rightleftharpoons \mathrm{RNHCH_2{-}O{-}CH_2NHR + H_2O}$$

Table 1. **Urea–Formaldehyde Reaction Rate Constants**

Reaction at 35°C and pH 4.0	k, L/(mol•s)
$\mathrm{U + F \rightarrow U/F}$	4.4×10^{-4}
$\mathrm{U/F + U \rightarrow U{-}CH_2U}$	3.3×10^{-4}
$\mathrm{U/F + U/F \rightarrow U{-}CH_2{-}U/F}$	0.85×10^{-4}
$\mathrm{U/F_2 + U/F \rightarrow FU{-}CH_2{-}U/F}$	0.5×10^{-4}
$\mathrm{U/F_2 + U/F_2 \rightarrow FU{-}CH_2{-}U/F_2}$	$<3\times10^{-6}$

The dimethylene ether so formed is less stable than the diamino–methylene bridge and may rearrange to form a methylene link and liberate a molecule of formaldehyde.

$$\mathrm{RNH{-}CH_2O{-}CH_2NHR \longrightarrow RNH{-}CH_2{-}NHR + HCHO}$$

The simple methylol compounds and the low molecular weight polymers obtained from urea and melamine are soluble in water and quite suitable for the manufacture of adhesives, molding compounds, and some kinds of textile treating resins. However, amino resins for coating applications require compatibility with the film-forming alkyd resins (qv) or copolymer resins with which they must react. Furthermore, even where compatible, the free methylol compounds are often too reactive and unstable for use in a coating-resin formulation that may have to be stored for some time before use. Reaction of the free methylol groups with an alcohol to convert them to alkoxy methyl groups solves both problems.

The replacement of the hydrogen of the methylol compound with an alkyl group renders the compound much more soluble in organic solvents and more stable. This reaction is also catalyzed by acids and usually carried out in the presence of considerable excess alcohol to suppress the competing self-condensation reaction. After neutralization of the acid catalyst, the excess alcohol may be stripped or left as a solvent for the amino resin.

The mechanism of the alkylation reaction is similar to curing. The methylol group becomes protonated and dissociates to form a carbonium ion intermediate that may react with alcohol to produce an alkoxymethyl group or with water to revert to the starting material. The amount of water in the reaction mixture should be kept to a minimum since the relative amounts of alcohol and water determine the final equilibrium.

Another way of achieving the desired compatibility with organic solvents is to employ an amino compound having an organic solubilizing group in the molecule, such as benzoguanamine. With one of the $-NH_2$ groups of melamine replaced with a phenyl group, benzoguanamine-formaldehyde resins [26160-89-4] have some degree of oil solubility even without additives. Nevertheless, benzoguanamine-formaldehyde resins are generally modified with alcohols to provide a still greater range of compatibility with solvent-based surface coatings. Benzoguanamine resins provide a high degree of detergent resistance together with good ductility and excellent adhesion to metal.

Displacement of a volatile with a nonvolatile alcohol is an important reaction for curing paint films with amino cross-linkers and amino resins on textile fabrics or paper. The following example is of a methoxymethyl group on an amino resin reacting with a hydroxyl group of a polymer chain.

$$\mathrm{RNHCH_2OCH_3 + HOCH_2{-} \longrightarrow RNHCH_2OCH_2{-} + CH_3OH}$$

A troublesome side reaction encountered in the manufacture and use of amino resins is the conversion of formaldehyde to formic acid. Often the reaction mixture of amino compound and formaldehyde must be heated under alkaline conditions. This favors a Cannizzaro reaction in which two molecules of formaldehyde interact to yield one molecule of methanol and one of formic acid.

$$2\,\mathrm{HCHO} + \mathrm{H_2O} \longrightarrow \mathrm{CH_3OH} + \mathrm{HCOOH}$$

Unless this reaction is controlled, the solution may become sufficiently acidic to catalyze the condensation reaction causing abnormally high viscosity or premature gelation of the resin solution.

4. Manufacture

Precise control of the course, speed, and extent of the reaction is essential for successful manufacture. Important factors are mole ratio of reactants; catalyst (pH of reaction mixture); and reaction time and temperature. Amino resins are usually made by a batch process. The formaldehyde and other reactants are charged to a kettle, the pH adjusted, and the charge heated. Often the pH of the formaldehyde is adjusted before adding the other reactants. Aqueous formaldehyde is most convenient to handle and lowest in cost.

In general, conditions for the first part of the reaction are selected to favor the formation of methylol compounds. After addition of the reactants, the conditions may be adjusted to control the polymerization. The reaction may be stopped to give a stable syrup. This syrup could be an adhesive or laminating resin and might be blended with filler to make a molding compound (see also LAMINATES; REINFORCED PLASTICS). It might also be an intermediate for the manufacture of a more complicated product, such as an alkylated amino resin, for use with other polymers in coatings.

The flow sheet (Fig. 2) illustrates the manufacture of amino resin syrups, cellulose-filled molding compounds, and spray-dried resins.

In the manufacture of amino resins, every effort is made to recover and recycle the raw materials. However, there may be some loss of formaldehyde, methanol, or other solvent as tanks and reactors are vented. Some formaldehyde, solvents, and alcohols are also evolved in the curing of paint films and the curing of adhesives and resins applied to textiles and paper. The amounts of material evolved in curing the resins may be small so that it may be difficult to justify the installation of complex recovery equipment. However, in the development of new resins for coatings and for treating textiles and paper, emphasis is being placed on those compositions that evolve a minimum of by-products on curing.

5. Uses

5.1. Adhesive Resins.

From antiquity, glues had been made almost entirely from materials of animal or vegetable origin, and were sensitive to moisture, oxidation, and bacterial or fungus attack. Because of these deficiencies, production of durable plywood, eg, was not possible. The modern plywood industry actually owes its growth to the availability of relatively low cost urea

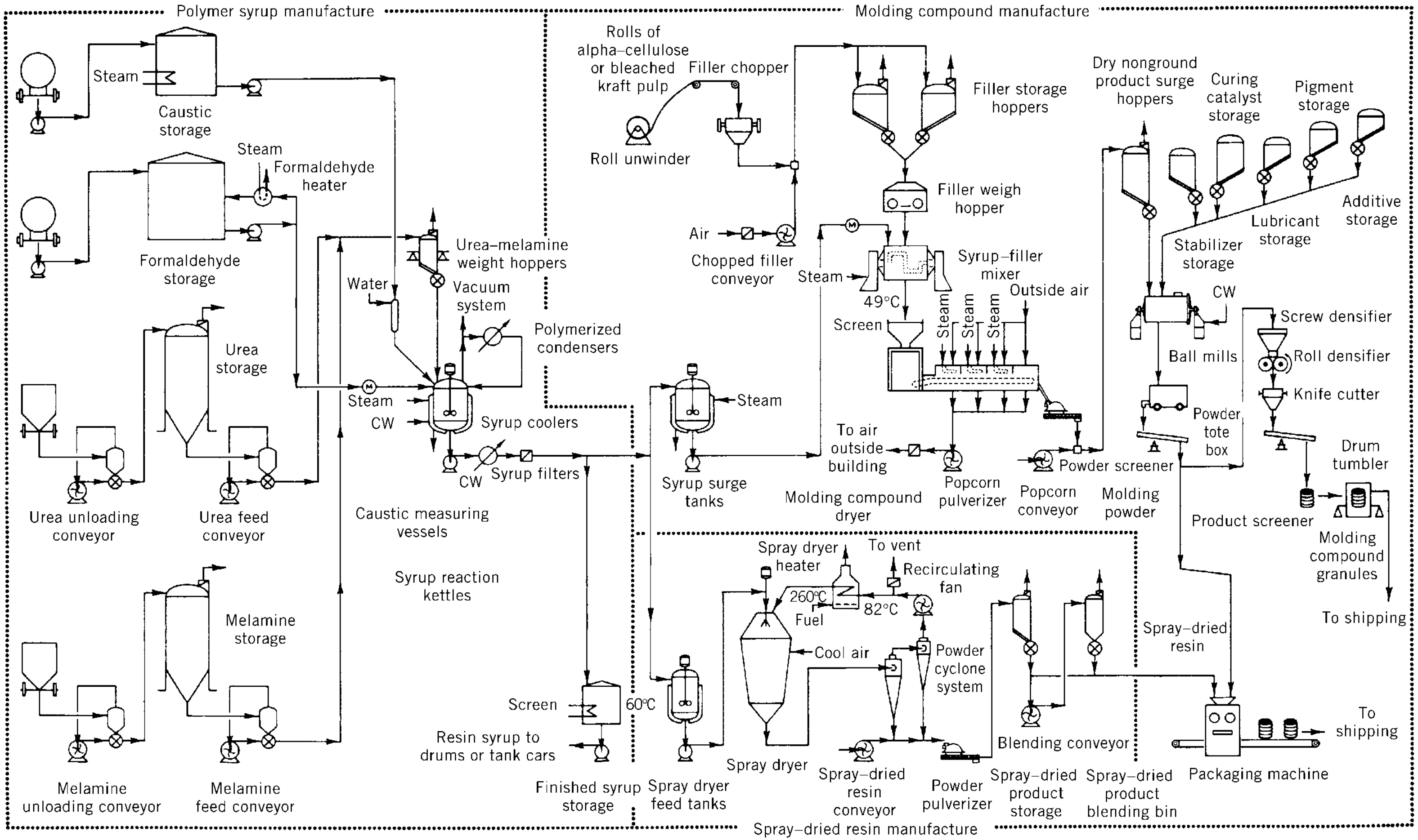


Fig. 2. Urea–formaldehyde and melamine–formaldehyde resin manufacture. CW = cold water. Courtesy of Stanford Research Institute.

adhesives. Plywood and chipboard or wood chip glues are often made at the plywood and chip board mill.

Urea and melamine adhesives represent products of very mature and overaged technologies. Essentially, they are simple reaction products of urea or melamine with formaldehyde; they may be liquids or powders. Liquids are converted to dry powders by "spray drying". Melamine–urea combinations generally are spray-dried powders of coreacted liquid melamine and urea-formaldehyde resins.

These adhesives are essentially for gluing wood. Urea–formaldehyde adhesives are used in the manufacture of plywood, in the fortification of starch adhesives for manufacture of paper bags and corrugated box boards, the production of "floral" and insulating foams, high quality sandpaper, and parquet flooring. Large volumes of urea resins are also sold in the United States for particle board bonding and other uses, at relatively low prices.

Melamine or melamine–ureas are used in the manufacture of truck and railroad flooring, laminated lumber, beams, exterior doors, marine plywood, toilet seats, and school furniture. The bonds in these products meet a variety of commercial, military, and federal specifications for exterior waterproof adhesives.

Ureas modified with furfuryl alcohol [98-00-0] find excellent acceptance for gluing or assembly of furniture, sporting goods, eg, tennis rackets, fishing rods, and water skiis, and for bonding decorative laminates to substrates such as particle board. Such ureas are called gap-filling adhesives. The modifier makes the resin less rigid, less highly cross-linked, and better able to relieve stresses imposed by shrinkage due to cure and loss of water in glue lines of nonuniform thickness.

In gluing, the adhesive must not saturate veneers or wood chips, but must remain in the glue line on the surface of the chips or between the plies. The adhesives are generally of high viscosity so that they remain in the glue line. Thickeners and extenders, such as powdered pecan shells and wheat flour, are often used.

Urea resin adhesives, by the use of the proper hardener, may be set either by heat or at room temperature. For room temperature curing, the hardener may be ammonium chloride, together with basic materials like calcium phosphate to neutralize excess acid that might damage the wood. Cold set or room temperature set adhesives are those that set satisfactorily at 20–30°C, whereas a hot set adhesive generally means one that is set $>99^\circ$C. Those that cure well between these temperatures are often referred to as intermediate set. Cold set types naturally set much faster at intermediate temperatures. Cold pressing of plywood is usually done in a hydraulic press. The press may then be opened, the clamped assembly removed, and allowed to stay under the pressure of the clamps for at least 4 h to set the glue.

Very rapid cures may be achieved by applying heat in the form of microwave radiation (see MICROWAVE TECHNOLOGY). The moist amino resin adhesive absorbs the high frequency radiation more readily than dry wood, thereby concentrating the heat in the glue line where it is needed. Hot pressing may be conducted in a hydraulic press comprising a large number of steam heated platens usually 5 cm thick. Pressures usually range from 1 to 2 MPa (150–300 psi). Hot press temperatures for urea and melamine–urea are usually 115–132°C.

In plywood production with ureas, the spread veneers should be pressed as soon as possible. The time between spreading and pressing, usually called assembly time, should never exceed 1 h. With some formulations, the permissible assembly time may be no >15 min. Melamine formulations and uncatalyzed melamine–urea combinations, however, can be spread and stored for as much as 1 week before use.

Ureas are not satisfactory for prolonged water immersion or for continuous exposure to warm and excessively humid conditions, although they are fairly resistant to normal humidity. Somewhat more durable bonds are obtained by heat setting. Ureas can be extended with wheat or rye flour, using as much as 150 parts flour to 100 parts dry resin. The extended glue still retains a fair degree of moisture resistance. Melamine resins have excellent water resistance, but cannot be cured at room temperature. Durable laminated wood beams used in building construction usually employ microwave technology for heat curing.

Continuous production of urea–formaldehyde resins has been described in many patents. In a typical example, urea and formaldehyde are combined and the solution pumped through a multistage unit. Temperature and pH are controlled at each stage to achieve the appropriate degree of polymerization. The product is then concentrated in a continuous evaporator to ~60–65% solids (31).

5.2. Laminating Resins. Phenolic and melamine resins are both used in the manufacture of decorative laminated plastic sheets for counters and table tops (see LAMINATES; REINFORCED PLASTICS). The phenolic is functional, being used in the backing or support sheets, whereas the melamine resin performs both decorative and functional roles in the print sheet and the protective overlay. Hardness, transparency, stain resistance, and freedom from discoloration are essential, in addition to a long-lasting working surface. Transparency is achieved because the refractive index of cured melamine-formaldehyde resin approaches that of the cellulose fibers and thus there is little scattering of light. Low cost and good mechanical properties are provided by the phenolic backing layers. In this instance, the combination of phenolic and amino resins achieves an objective that neither would normally be capable of performing alone. Developments in modified melamine resins have contributed to commercialization of premium priced through-color decorative laminates in which the dark color phenolic backing layers are replaced by color layers matching the full range of surface colors.

Phenolic resins are generally used in alcoholic solution, whereas melamine resins are best handled in water or water–alcohol mixtures. The paper or cloth web is passed through a dip tank containing resin solution, adjusted for pick-up on squeeze rolls, and then passed through a heated drying oven. Once dried, the treated paper or cloth is fairly stable and, stored in a cool place, it may be kept for several weeks or months before pressing into laminated plastic sheets.

A melamine laminating resin used to saturate the print and overlay papers of a typical decorative laminate might contain 2 mol of formaldehyde for each mole of melamine. In order to inhibit crystallization of methylol melamines, the reaction is continued until about one-fourth of the reaction product has been converted to low molecular weight polymer. A simple determination of free formaldehyde may be used to follow the first stage of the reaction, and the build-up of polymer in the reaction mixture may be followed by cloud-point dilution or viscosity tests.

A particularly interesting and useful test is run at high dilution. One or two drops of resin are added to a test tube half full of water. A cloudy streak as the drop sinks through the water indicates that the resin has advanced to the point where the highest molecular weight fraction of polymer is no longer soluble in water at that particular temperature. At this high dilution, the proportion of water to resin is not critical, hence the only measurement needed is the temperature of the water. The temperature at or below which the drops give a white streak is known as the hydrophobe temperature. This test is particularly useful with melamine resins.

Laminates are pressed in steam-heated, multiple-opening presses. Each opening may contain a book of as many as 10 laminates pressed against polished steel plates. Curing conditions are 20–30 min at ~150°C under a pressure of ~6900 kPa (1000 psi).

5.3. Molding Compounds. Molding was the first big application for amino resins, although molding compounds are more complex than either laminating resins or adhesives. A simple amino resin molding compound might be made by combining melamine with 37% formalin in the ratio of 2 mol of formaldehyde for each mole of melamine at neutral or slightly alkaline pH and a temperature of 60°C. The reaction should be continued until some polymeric product has been formed to inhibit crystallization of dimethylolmelamine upon cooling. When the proper reaction stage has been reached, the resin syrup is pumped to a dough mixer where it is combined with alpha-cellulose pulp, approximately one part of cellulose to each three parts of resin solids. The wet, spongy mass formed in the dough mixer is then spread on trays where it is combined with alpha-cellulose in a humidity-controlled oven to produce a hard, brittle popcorn-like intermediate. This material may be coarsely ground and sent to storage. To make the molding material, the cellulose–melamine resin intermediate is combined in a ball mill with a suitable catalyst, stabilizer, colorants, and mold lubricants. The materials must be ground for several hours to achieve the uniform fine dispersion needed to get the desired decorative appearance in the molded article. The molding compound may be used as a powder or it may be compacted under heat and pressure to a granular product that is easier to handle (32). A urea molding compound might be made in much the same way using a resin made with 1.3–1.5 mol of formaldehyde per 1.0 mol of urea.

Amino molding compounds can be compression, injection, or transfer molded. Urea molding compound has found wide use and acceptance in the electrical surface wiring device industry. Typical applications are circuit breakers, switches, wall plates, and duplex outlets. Urea is also used in closures, stove hardware, buttons, and small housings. Melamine molding compound is used primarily in dinnerware applications for both domestic and institutional use. It is also used in electrical wiring devices, ashtrays, buttons, and housings.

The emergence of a new amino application is rare at this point in its relatively long life, but one such has appeared and is growing rapidly. Because of the relative hardness of both urea and melamine moldings, a unique use has been developed for small, granular sized particles of cut up molded articles. It is the employment of a pressurized stream of plastic particles to remove paint without damaging the surface beneath, and can be compared to a sandblasting operation. This procedure is gaining wide acceptance by both commercial airlines and the military for the refinishing of painted surfaces. It does not harm the substrate and eliminates the use of chemicals formerly used in stripping paint.

To speed up the molding process, the required amount of molding powder or granules is often pressed into a block and prewarmed before placing it in the mold. Rapid and uniform heating is accomplished in a high frequency preheater; essentially an industrial microwave oven. The prewarmed block is then transferred to the hot mold, pressed into shape, and cured.

Production of decorated melamine plastic dinner plates makes use of molding and laminating techniques. The pattern is printed on the same type of paper used for the protective overlay of decorative laminates, treated with melamine resin and dried, and then cut into disks of the appropriate size.

To make a decorated plate, the mold is opened shortly after the main charge of molding compound has been pressed into shape, the decorative foil is laid in the mold on top of the partially cured plate, printed side down, and the mold closed again to complete the curing process. The melamine-treated foil is thus fused to the molded plate and, as with the decorative laminate, the overlay becomes transparent so that the printed design shows through yet is protected by the film of cured resin.

The excellent electrical properties, hardness, heat resistance, and strength of melamine resins makes them useful for a variety of industrial applications. Some representative properties of amino resin molding compounds, including the industrial-grade melamines, are listed in Table 2.

In 1989 quantity costs, which reflect the lowest cost, of urea molding compounds were ~\$1.41/kg (\$0.035/in.^{3}) for black and brown colors, \$1.58/kg (\$0.039/in.^{3}) for white and ivory; special colors are somewhat higher in price. The approximate cost of cellulose-filled melamine molding compound is \$1.74/kg (\$0.043/in.^{3}). Glass fiber-filled melamine sells for \$7.70/kg (\$0.22/in.^{3}).

Amino molding compounds are produced worldwide. The following list represents the major suppliers.

Company	Location	Product
American Cyanamid	USA	urea melamine
BIP Chemical	England	urea melamine
Budd Chemical	USA	urea
Carmel Chemical	Israel	urea melamine
Fiberite	USA	melamine
Perstrop	Sweden USA	urea melamine
Plastics Mfg. Co.	USA	urea melamine
Plastics Engineering Co.	USA	melamine

Table 2. **Typical Properties of Filled Amino Resin Molding Compounds**

ASTM or UL test	Property	Urea	Melamine		
		Alpha-cellulose	Alpha-cellulose	Macerated fabric	Glass fiber
		Physical			
D792	specific gravity	1.47–1.52	1.47–1.52	1.5	1.8–2.0
D570	water absorption, 24 h, 3.2 mm thick, %	0.48	0.1–0.6	0.3–0.6	0.09–0.21
		Mechanical			
D638	tensile strength, MPa^a	38–48	48–90	55–69	35–70
D638	elongation, %	0.5–1.0	0.6–0.9	0.6–0.8	
D638	tensile modulus, GPa^b	9–9.7	9.3	9.7–11	16.5
D785	hardness, Rockwell M	110–120	120	120	115
D790	flexural strength, MPa^a	70–124	83–104	83–104	90–165
D7900	flexural modulus, GPa^b	9.7–10.3	7.6	9.7	16.5
D256	impact strength, J/m^c of notch	14–18	13–19	32–53	32–1000
		Thermal			
C177	thermal conductivity, 10^{-4} W/(m·K)	42.3	29.3–42.3	44.3	48.1
D696	coefficient of thermal expansion, 10^{-5} cm/(cm·°C)	2.2–3.6	2.0–5.7	2.5–2.8	1.5–1.7
D648	deflection temperature at 1.8 MPa^a, °C	130	182	154	204
UL 94	flammability class	VO^d	VO^d		VO
	continuous no-load service temperature, °C	77^e	99^e	121	149–204

		Electrical			
D149	dielectric strength, V/0.00254 cm				
	short time, 3.2 mm thick	330–370	270–300	250–350	170–300
	step by step	220–250	240–270	200–300	170–240
D150	dielectric constant, 22.8°C				
	at 60 Hz	7.7–7.9	8.4–9.4	7.6–12.6	9.7–11.1
	at 10^3 Hz		7.8–9.2	7.1–7.8	
D150	dissipation factor, 22.8°C				
	at 60 Hz	0.034–0.043	0.030–0.083	0.07–0.34	0.14–0.23
	at 10^3 Hz		0.015–0.036	0.03–0.05	
D257	volume resistivity, 22.8°C, 50% rh, Ω·cm	$0.5 - 5.0 \times 10^{11}$	$0.8 - 2.0 \times 10^{12}$	$1.0 - 3.0 \times 10^{11}$	$0.9 - 2.0 \times 10^{11}$
D495	arc resistance, s	80–100	125–136	122–128	180–186

[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 145,000.

[c] To convert J/m to ftlbf/in., divide by 53.38.

[d] Applies to specimens thicker than 1.6 mm.

[e] Based on no color change.

5.4. Coatings. Cured amino resins are far too brittle to be used alone as surface coatings for metal or wood substrates, but in combination with other film formers (alkyds, polyesters, acrylics, epoxies) a wide range of acceptable performance properties can be achieved. These combination binder coating formulations cure rapidly at slightly elevated temperatures, making them well suited for industrial baking applications. The amino resin content in the formulation is typically in the range of 10–50% of the total binder solids.

A wide selection of amino resin compositions is commercially available. They are all alkylated to some extent in order to provide compatibility with the other film formers, and formulation stability. They vary not only in the type of amine (melamine, urea, benzoguanamine, and glycoluril) used, but also in the concentration of combined formaldehyde, and the type and concentration of alkylation alcohol (*n*-butanol, isobutyl alcohol, methanol).

On curing, amino resins not only react with the nucleophilic sites (hydroxyl, carboxyl, amide) on the other film formers in the formulation, but also self-condense to some extent. Highly alkylated amino resins have less tendency to self-condense (33,34). Therefore they are effective cross-linking agents, but may require the addition of a strong acid catalyst to obtain acceptable cure even at bake temperatures of 120–177°C.

Amino resins based on urea have advantages in low temperature cure response and low cost. However, they are not as stable to ultraviolet (uv) radiation as melamine resins, and have poorer heat resistance; therefore, they have been successful primarily in interior wood finishes. Melamine resins, on the other hand, are uv stable, have excellent heat resistance, film hardness, and chemical resistance. They therefore dominate amino resin usage in (OEM) automotive coatings, general metals finishes, container coatings (both interior and exterior), and prefinished metal applications. Glycoluril resins have also found use in prefinished metal, primarily because of their high film flexibility properties. Unalkylated glycoluril resins are unique in that they are stable under slightly acidic conditions and have therefore found use in low temperature cure waterborne finishes. Benzoguanamine resins have historically been successful in appliance finishes because of their superior chemical resistance and specifically their detergent resistance. However, they have both poor uv resistance and economics, which have limited their use in other application areas.

When first introduced to the coatings industry, amino resin compositions were partially butylated and relatively polymeric in nature, with degrees of polymerization of 4–6. However, the dominant amino resin in today's industrial coating is based on a highly methylated, highly monomeric (degrees of polymerization of 1.4–2.6) melamine cross-linking agent. Variations of extent of methylolation and methylation exist along with a number of co-ethers where the melamine molecule is both methylated and either *n*-butylated or isobutylated. This type of composition dominates because it best addresses the pollution (low volatile organic compounds) and performance requirements of today's industrial finishes (see COATINGS, INDUSTRIAL).

Methylation provides fast cure response, improved exterior exposure, high weight retention on curing, and suitability for both solvent and waterborne systems. Waterborne systems, in most instances, provide lower pollution than solvent-based formulations. High monomer content reduces the viscosity of the amino resin, again lowering pollution particularly when used in solvent-based systems, and also improves film flexibility, and recoat adhesion. When some butylation is included as part of the alkylation, the viscosity of the amino resin is lowered, thereby lowering pollution (of the formulated coating), improving recoat adhesion, and improving wetting and flow characteristics. An amino resin is usually selected based on specific performance properties required or performance to be emphasized.

Stability in storage is an important property for coating systems containing amino resins. If the amino resin undergoes self-condensation or reacts at room temperature with the alkyd or other film-forming polymer, the system may become too viscous or thicken to a gel that can no longer be used for coating. Alkyds usually contain sufficient free carboxyl groups to catalyze the curing reaction when the coating is baked, but this may also cause the paint to thicken in storage. Partial neutralization of the acid groups with an amine can greatly improve storage stability yet allow the film to cure when baked, since much of the amine is vaporized with the solvent during the baking process. 2-Amino-2-methyl-1-propanol [124-68-5], triethylamine [121-44-8], and dimethylaminoethanol [108-01-1] are commonly used as stabilizers. Alcohols as solvent also improve storage stability. Catalyst addition just before the coating is to be applied permits rapid curing and avoids the problem of storage stability. A strong acid soluble in organic solvents such as *p*-toluenesulfonic acid is very effective and may be partially neutralized with an amine to avoid premature reaction.

A butylated urea–formaldehyde resin for use in the formulation of fast-curing baking enamels might be made beginning with the charge: urea (1.0 mol), paraformaldehyde (2.12 mol), and butanol (1.50 mol). Triethanolamine is added to make the solution alkaline ($\sim$1% of the weight of the urea) and the mixture is refluxed until the paraformaldehyde is dissolved. Phthalic anhydride is added to give a pH of 4.0 and the water is removed by azeotropic distillation until the batch temperature reaches 117°C. Cooling and dilution with solvent is done until the desired solids content is reached (35).

A highly methylated melamine–formaldehyde resin for cross-linking with little or no self-condensation might be made as follows (36). A solution of formaldehyde in methanol is charged to a reaction kettle and adjusted to a pH of 9.0–9.5 using sodium hydroxide. Melamine is then added to give a ratio of 1 mol of melamine for each 6.5 mol of formaldehyde and the mixture refluxed for ½ h. The reaction is then cooled to 35°C and more methanol added to bring the ratio of methanol per mole of melamine up to 11. With the batch temperature at 35°C, enough sulfuric acid is added to reduce the pH to 1.0. After holding the reaction mixture at this temperature and pH for 1 h, the batch is neutralized with 50% sodium hydroxide and the excess methanol stripped to give a product containing 60% solids which is then clarified by filtration. A highly methylated resin, such as this, may be used in water-based (37) or solvent-type coatings. It might also be used to provide crease resistance to cotton fabric.

The principal problems facing amino resins in the industrial coatings of the 1990s are formaldehyde emission and low temperature cure performance. Significant progress has been made in reducing the residual free formaldehyde in the amino resin, but formaldehyde generation on baking must still be addressed. Concerning low temperature cure performance, emphasis is being placed on catalyst selection. Amino resins cure at bake temperatures as low as 71–82°C, but at these bake temperatures they require high concentrations of acid catalyst, which negatively affect hydrolysis resistance or water sensitivity of the cured film. The development of improved catalysts is the most promising solution to low temperature cure performance enhancement.

5.5. Textile Finishes. Most amino resins used commercially for finishing textile fabrics are methylolated derivatives of urea or melamine. Although these products are usually monomeric, they may contain some polymer by-product.

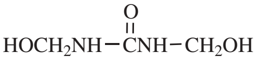
Amino resins react with cellulosic fibers and change their physical properties. They do not react with synthetic fibers, such as nylon, polyester, or acrylics, but may self-condense on the surface. This results in a change in the stiffness or resiliency of the fiber. Partially polymerized amino resins of such molecular size that prevents them from penetrating the amorphous portion of cellulose also tend to increase the stiffness or resiliency of cellulose fibers.

Monomeric amino resins react predominantly with the primary hydroxyls of the cellulose, thereby replacing weak hydrogen bonds with strong covalent bonds which leads to an increase in fiber elasticity. When an untreated cotton fiber is stretched or deformed by bending, as in forming a crease or wrinkle, the relatively weak hydrogen bonds are broken and then reform to hold the fiber in its new position. The covalent bonds that are formed when adjacent cellulose chains are cross-linked with an amino resin are five to six times stronger than the hydrogen bonds. Covalent bonds are not broken when the fiber is stretched or otherwise deformed. Consequently, the fiber tends to return to its original condition when the strain is removed. This increased elasticity is manifested in two important ways: (*1*) When a cotton fabric is cross-linked while it is held flat, the fabric tends to return to its flat condition after it has been wrinkled during use or during laundering. Garments made from this type of fabric are known as wash-and-wear, minimum care, or no-iron. (*2*) A pair of pants that is pressed to form a crease and then cross-linked tends to maintain the crease through wearing and laundering. This type of garment is called durable-press or permanent press (see TEXTILES).

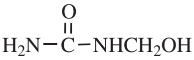
This increased elasticity is always accompanied by a decrease in strength of the cellulose fiber that occurs even though weak hydrogen bonds are replaced by stronger covalent bonds. The loss of strength is not caused by hydrolytic damage to the cellulose. If the cross-linking agent is removed by acid hydrolysis, eg, the fiber will regain most, if not all, of its original strength. The loss in strength is believed to be due to intramolecular reaction of the amino resin along the cellulose chain to displace a larger number of hydrogen bonds, resulting in a net loss in strength. The intramolecular and intermolecular reactions (cross-linking) both occur at the same time.

Although there are many different amino resins used for textile finishing, all of them impart about the same degree of increase in elasticity when applied on an equal molar basis. Elasticity can be measured by determining the recovery from wrinkling. Although all these products impart about the same degree of improvement in elasticity, they also may impart many other desirable or undesirable properties to the fabric. The development of amino resins for textile finishing has been aimed toward maximizing the desirable properties and minimizing the undesirable ones. Most of the resins and reactants used in today's textile market are based on urea as a starting material. However, the chemistry differs considerably from that employed in early textile-finishing operations.

The first amino resins used commercially on textiles were the so-called urea–formaldehyde resins, dimethylolurea [140-95-4], or its mixtures with monomethylolurea [1000-82-4].



$$HOCH_2NH{-}\overset{\overset{O}{\|}}{C}NH{-}CH_2OH$$



$$H_2N{-}\overset{\overset{O}{\|}}{C}{-}NHCH_2OH$$

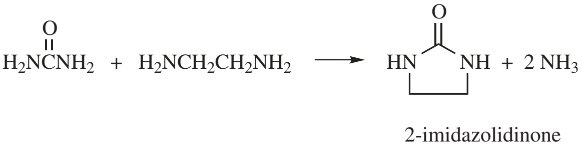
Their performance falls short of most present finishes, particularly in durability, resistance to chlorine-containing bleaches, and formaldehyde release, and they are not used much today. Both urea and formaldehyde are relatively inexpensive, and manufacture is simple; ie, 1–2 mol of formaldehyde as an aqueous solution reacts with 1 mol of urea under mildly alkaline conditions at slightly elevated temperatures.

Since the methylolurea monomers have limited water solubility (∼30%), they were usually marketed in dispersed form as soft pastes containing 55–65% active ingredient in order to decrease container and shipping costs. By increasing the temperature and using slightly acid conditions, dimethylolureas can be made as a series of short polymers that have infinite water solubility and can be marketed at concentrations as high as 85%. However, because these result in increased fabric stiffness, they cannot be used interchangeably with the monomeric materials. Both forms polymerize readily in storage and, unless kept under refrigeration, become water insoluble within a few weeks at ambient temperatures.

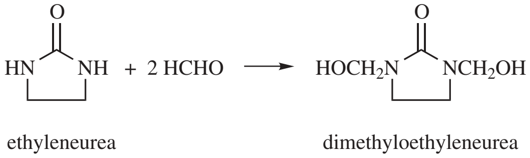
To overcome stability and water solubility problems, methylolurea resins are frequently alkylated to block the reactive hydroxyl groups. For reasons of economy, the alkylating agent is usually methanol. In this process, 2 mol of aqueous formaldehyde reacts with 1 mol of urea under alkaline conditions to form dimethylolurea. Excess methanol is then added, and the reaction is continued under acid conditions to form methoxymethylurea. Both methylol groups can be methylated by maintaining low concentrations of water and using a large excess of methanol; however, methylation of only one of the methylol groups is sufficient to provide adequate shelf life and water solubility. Upon completion of the methylation reaction, the resin is adjusted to pH 7–10, and excess methanol and water are removed by distillation under reduced pressure to provide syrups of 50–80% active ingredients.

Like methylolureas, cyclic ureas are based on reactions between urea and formaldehyde; however, the amino resin is cyclic rather than linear. Many cyclic urea resins have been used in textile-finishing processes, particularly to achieve wrinkle resistance and shrinkage control, but the ones described below are the most commercially important. They are all in use today to greater or lesser extents, depending on specific end requirements (see also TEXTILES, FINISHING).

Ethyleneurea Resins. One of the most widely used resins during the 1950s and 1960s was based on dimethylolethyleneurea [136-84-5] (1,3-bis(hydroxymethyl)-2-imidazolidinone) commonly known as ethyleneurea resin. This resin [28906-87-8] is most conveniently prepared from urea, ethylenediamine, and formaldehyde. 2-Imidazolidinone [120-93-4] (ethyleneurea) is first prepared by the reaction of excess ethylenediamine [107-15-3] with urea (38) in an aqueous medium at ∼116°C.

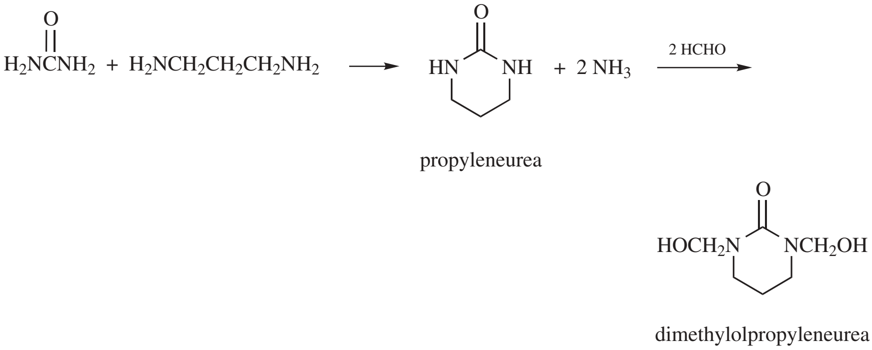


A fractionating column is required for the removal of ammonia and recycle of ethylenediamine. The molten product (mp 133°C) is then run into ice water to give a solution that is methylolated with 37% aqueous formaldehyde.



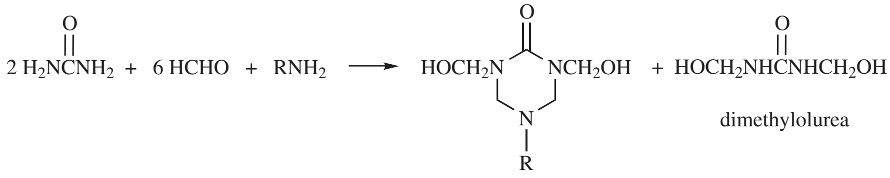
The resin, generally a 50% solution in water, has excellent shelf life and is stable to hydrolysis and polymerization.

Propylene Urea Resins. In similar fashion to ethyleneurea, dimethylolpropyleneurea [3270-74-4] [1,3-bis(hydroxymethyl)tetrahydro-2-(1*H*)-pyrimidinone] is the basis of propyleneurea–formaldehyde resin [65405-39-2]. Its preparation is from urea, 1,3-diaminopropane [109-76-2], and formaldehyde.



This resin was temporarily accepted, primarily because of its improved resistance to acid washes. However, the relatively high cost of the diamine precluded widespread commercial acceptance.

Triazone. Triazone is the common name for the class of compounds corresponding to the dimethylol derivatives of tetrahydro-5-alkyl-*s*-triazone. They can be made readily and cheaply from urea, formaldehyde, and a primary aliphatic amine. A wide variety of amines may be used to form the six-membered ring (39); however, for reasons of cost and odor, hydroxyethylamine (monoethanolamine) is used preferentially (see ALKANOLAMINES). Since the presence of straight-chain methylolureas causes no deleterious effects to the fabric finish, the triazones typically are prepared with less than the stoichiometric quantity of the amine. This results not only in a less costly resin but also in improved performance (40).

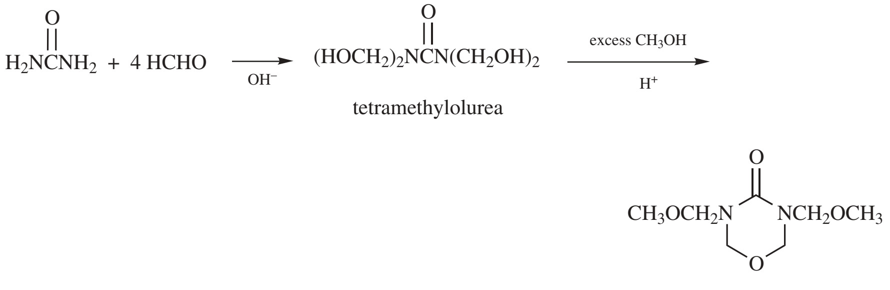


dimethylolurea

1,3-bis(hydroxymethyl)tetrahydro-5-alkyl-*s*-triaz-2-one

The resin is simply prepared by heating the components together. Usually the urea and formaldehyde are first charged to the kettle and heated under alkaline conditions to give a mixture of polymethylolureas, followed by the slow addition of the amine with continued heating to form the cyclic compound. The order of addition can be varied as can the molar ratios to yield a range of chain-ring compound ratios. The commercial resin is usually sold as a 50% solids solution in water.

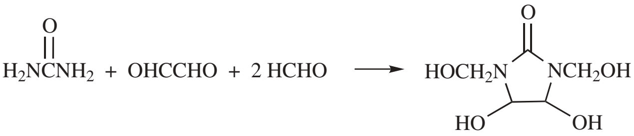
Uron Resins. In the textile industry, the term uron resin usually refers to the mixture of a minor amount of melamine resin and so-called uron, which in turn is predominantly *N,N′*-bis(methoxymethyl)uron [7388-44-5] plus 15–25% methylated urea–formaldehyde resins, a by-product. *N,N′*-bis(methoxymethyl)-uron was first isolated and described in 1936 (41), but was commercialized only in 1960. It is manufactured (42) by the reaction of 4 mol of formaldehyde with 1 mol of urea at 60°C under highly alkaline conditions to form tetramethylolurea [2787-01-1]. After concentration under reduced pressure to remove water, excess methanol is charged and the reaction is continued under acidic conditions at ambient temperatures to close the ring and methylate the hydroxymethyl groups. After filtration to remove the precipitated salts, the methanolic solution is concentrated to recover excess methanol. The product (75–85% pure) is then mixed with a methylated melamine–formaldehyde resin to reduce fabric strength losses in the presence of chlorine, and diluted with water to 50–75% solids. Uron resins do not find significant use today due to the greater amounts of formaldehyde released from fabric treated with these resins.



tetramethylolurea

N,*N*′ -bis(methoxymethyl)uron

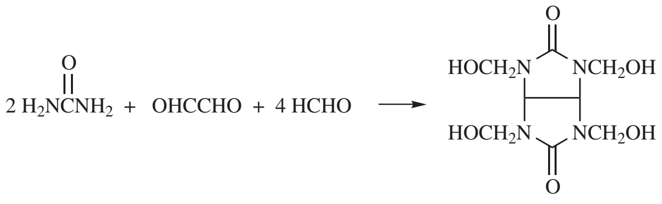
Glyoxal Resins. Since the late 1960s, glyoxal resins have dominated the textile-finish market for use as wrinkle-recovery, wash-and-wear, and durable-press agents. These resins are based on 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone, commonly called dimethyloldihydroxyethyleneurea [1854-26-8] (DMDHEU). Several methods of preparation are described in the literature (43). On a commercial scale, DMDHEU can be prepared inexpensively at high purity by a one-kettle process (44): 1 mol of urea, 1 mol of glyoxal [107-22-2] as 40% solution, and 2 mol of formaldehyde in aqueous solution are charged to the reaction vessel. The pH is adjusted to 7.5–9.5 and the mixture heated at 60–70°C. The reaction is nearly stoichiometric; excess reagent is not necessary.



DMDHEU

Glyoxal resins are generally sold at 45% solids solutions in water. Resin usage for crease-resistant fabrics had increased to well over 60×10^6 kg by 1974 and over one-half of this was DMDHEU for durable-press garments. In the early 1980s, glyoxal resins modified with diethylene glycol [111-46-6] became prominent in the marketplace. These products are either simple mixtures of diethylene glycol and DMDHEU in water solution or the reaction product of diethylene glycol and DMDHEU. Rarely, ethylene glycol has been used in place of diethylene glycol. The diethylene glycol modified DMDHEU products have the advantage of releasing significantly less formaldehyde from the finished fabric after resin curing than fabric treated with DMDHEU. On the other hand, durable-press performance and shrinkage control are somewhat less with the glycol modified resins.

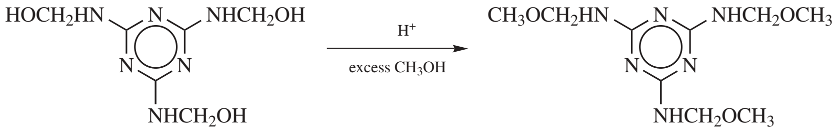
A less important glyoxal resin is (tetramethylolacetylenediurea) tetramenthylolglycoluril [5395-50-6] produced by the reaction of 1 mol of glyoxal with 2 mol of urea, and 4 mol of formaldehyde.



tetramethylolglycoluril

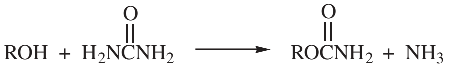
This resin was most popular in Europe, partly because of its lower requirements of glyoxal. However, because of increased availability and lower glyoxal costs plus certain application weaknesses, it has been generally replaced by DMDHEU.

Melamine–Formaldehyde Resins. The most versatile textile-finishing resins are the melamine–formaldehyde resins. They provide wash-and-wear properties to cellulosic fabrics, and enhance the wash durability of flame-retardant finishes. Butylated melamine–formaldehyde resins of the type used in surface coatings may be used in textile printing-ink formulations. A typical textile melamine resin is the dimethyl ether of trimethylolmelamine [1852-22-8] that can be prepared as follows:



Under alkaline conditions, 3 mol of formaldehyde react with 1 mol of melamine at elevated temperatures. Since water interferes with the methylation, methylolation is carried out in methanol with paraformaldehyde and by simply adjusting the pH to ~4 with continued heating. After alkylation is complete the pH is adjusted to 8–10 and excess methanol is distilled under reduced pressure. The resulting syrup contains ~80% solids.

Miscellaneous Resins. Much less important than the melamine–formaldehyde and urea–formaldehyde resins are the methylol carbamates. They are urea derivatives since they are made from urea and an alcohol (R can vary from methyl to a monoalkyl ether of ethylene glycol).



$$ROH + H_2N\overset{\overset{O}{\|}}{C}NH_2 \longrightarrow RO\overset{\overset{O}{\|}}{C}NH_2 + NH_3$$

Temperatures >of 140°C are required to complete the reaction and pressurized equipment is used for alcohols boiling below this temperature; provision must be made for venting ammonia without loss of alcohol. The reaction is straightforward and, in the case of the monomethyl ether of ethylene glycol [109-86-4], can be carried out at atmospheric pressure using stoichiometric quantities of urea and alcohol (45). Methylolation with aqueous formaldehyde is carried out at 70–90°C under alkaline conditions. The excess formaldehyde needed for complete dimethylolation remains in the resin and prevents more extensive usage because of formaldehyde odor problems in the mill.

Other amino resins used in the textile industry for rather specific properties have included the methylol derivatives of acrylamide (46), hydantoin [461-79-3] (47), and dicyandiamide (48).

Textiles are finished with amino resins in four steps. The fabric is (*1*) passed through a solution containing the chemicals, (*2*) through squeeze rolls (padding) to remove excess solution, (*3*) dried, and (*4*) heated (cured) to bond the chemicals with the cellulose or to polymerize them on the fabric surface.

The solution (pad bath) contains one or more of the amino resins described above, a catalyst, and other additives such as a softener, a stiffening agent, or a water repellant. The catalyst may be an ammonium or metal salt, eg, magnesium chloride or zinc nitrate. Synthetic fabrics, such as nylon or polyester, are treated with amino resins to obtain a stiff finish. Cotton (qv) or rayon fabrics or blends with synthetic fibers are treated with amino resins to obtain shrinkage control and a durable-press finish.

Normally, fabrics are treated in the sequence outlined above. The temperature of the drying unit is 100–110°C and the temperature of the curing unit can vary between 120 and 200°C but usually ranges from 150 to 180°C. The higher temperatures are employed to polymerize the resins on synthetic fabrics and at the same time to heat-set the fibers. Temperatures up to 180°C are used to allow the amino resins to react with cellulosic fibers alone or blended with synthetic fibers. The fabric is held flat but with minimum tension during drying and curing and always tends to become flat when creased or wrinkled during use or laundering. The resin-treated cellulose absorbs less water and swells less than untreated cellulose. This reduced swelling along with little or no tension induced during drying minimizes shrinkage during laundering.

The steps followed in the precure are repeated in the postcure process, except that after the drying step the goods are shipped to a garment manufacturer who makes garments, presses them into the desired shape with creases or pleats, and then cures the amino resin on the completed garment. It is important that the amino resins used in the postcure process should (*1*) not react with the fabric before it has been fashioned into a garment, and (*2*) release a minimum amount of formaldehyde into the atmosphere, especially while the goods are in storage or during the cutting and sewing operations. These requirements are met, at present, with the diethylene glycol modified DMDHEU resin.

Tire Cord. Melamine resins are also used to improve the adhesion of rubber to reinforcing cord in tires. Textile cord is normally coated with a latex dip solution composed of a vinylpyridine–styrene–butadiene latex rubber containing resorcinol–formaldehyde resin. The dip coat is cured prior to use. The dip coat improves the adhesion of the textile cord to rubber. Further improvement in adhesion is provided by adding resorcinol and hexa(methoxymethyl) melamine (HMMM) [3089-11-0] to the rubber compound that is in contact with the textile cord. The HMMM resin and resorcinol cross-link during rubber vulcanization and cure to form an interpenetrating polymer within the rubber matrix that strengthens or reinforces the rubber and increases adhesion to the textile cord. Brass-coated steel cord is also widely used in tires for reinforcement. Steel belts and bead wire are common applications. Again, HMMM resins and resorcinol [108-46-3] are used in the rubber compound which is in contact with the steel cord to reinforce the rubber and increase the adhesion of the rubber to the steel cord. This use of melamine resins is described in the patent literature (49).

5.6. Amino Resins in the Paper Industry.

Paper (qv) is a material of tremendous versatility and utility, prepared from a renewable resource. It may be made soft or stiff, dense or porous, absorbent or water repellent, textured or smooth. Some of the versatility originates with the fibers, which may vary from short and supple to long and stiff, but the contribution of chemicals should not be underestimated (see PAPERMAKING MATERIALS AND ADDITIVES).

Amino resins are used by the paper industry in large volume for a variety of applications. The resins are divided into two classes according to the mode of application. Resins added to the fiber slurry before the sheet is formed are called wet-end additives and are used to improve wet and dry strength and stiffness. Resins applied to the surface of formed paper or board, almost invariably together with other additives, are used to improve the water resistance of coatings, the sag resistance in ceiling tiles, and the scuff resistance in cartons and labels.

The requirements for the two types of resins are very different. Wet-end additives are used in dilute fiber slurries in small amounts. After the sheet is formed, most of the water is drained away and some of the remaining water is pressed out of the sheet before it is dried. The amino resin must be retained (absorbed) on the surface of the cellulose fibers so that it will not be washed away. On a typical paper machine, fiber concentration in the headbox would be $\sim$1%. If the amount of wet-strength resin used is 1% of the weight of the fiber, the concentration of resin in the headbox would be only 0.01%. If no mechanism for attaching the resin to the fiber is provided, only a trace of the resin added to the slurry would be retained in the finished sheet. Good retention is achieved with the amino resin by making the resin cationic. Since the cellulose surface is anionic because of the carboxylic acid groups present, the cationic charge on the resin makes it substantive with the fiber leading to good retention of the resin when applied in the wet-end. Resins for application to the surface of preformed paper are not required to be substantive to cellulose and they may be formulated for adhesion, cure rate, viscosity, compatibility with other materials, etc, without concern for retention.

The integrity of a paper sheet is dependent on the hydrogen bonds that form between the fine structures of cellulose fibers during the pressing and drying operations (see CELLULOSE). The bonds between hydroxyl groups of neighboring fibers are very strong when the paper is dry but are severely weakened as soon as the paper becomes wet. Bonding between the hydroxyls of cellulose and water is as energetic as bonding between two cellulose hydroxyl groups. Consequently, ordinary paper loses most of its strength when it is wet or exposed to very high humidity. The sheet loses its stiffness and bursting, tensile, and tearing strength.

Many materials have been used over the years in an effort to correct this weakness in paper. If water can be prevented from reaching the sites of the bonding by sizing or coating the sheet, then a measure of wet strength may be attained. Water molecules are so small and cellulose so hydrophilic that this solution usually affords only temporary protection. Formaldehyde, glyoxal, polyethylenimine, and, more recently, derivatized starch (50) and derivatized cationic polyacrylamide resins (51) have been used to provide temporary wet strength. The first two materials must be applied to the formed paper but the other materials are substantive to the fiber and may be used as wet-end additives. Carboxymethyl–cellulose– calcium chloride and locust bean gum–borax are examples of two-component systems applied separately to paper that were used to a limited extent before the advent of the amino resins. Today three major types of wet-strength resins are used in papermaking: polyamide–polyamine resins cross-linked with epichlorohydrin (52) are used in neutral to alkaline papers; cationic polyacrylamide resins cross-linked with glyoxal are used for acid to neutral papers; and melamine–formaldehyde resins are used for acid papers.

During the thirty year period following the introduction of synthetic wet-strength additives to papermaking in 1942, most paper was made at acid pH. Low molecular weight (or even monomeric) trimethylolmelamine [1017-56-7], when dissolved in the proper amount of dilute acid and aged, polymerizes to a colloidal polymer that is retained well by almost all types of papermaking fiber, and produces high wet strength under the mild curing conditions easily attained on a paper machine (53, 54). This resin, introduced by American Cyanamid in 1942, is still extensively used when rapid cure, high wet strength, and good dry strength are important in acid paper. Some processing improvements have been made, including a report (55) describing the formation of a stable melamine resin acid colloid using formic and phosphoric acids. The chemistry of this reaction is quite interesting.

Melamine–formaldehyde acts as an amine when dissolved in dilute acid, usually hydrochloric acid (HCl). During polymerization, between 20 and 80 monomeric units combine to form a polymer of colloidal dimensions (6–30 nm) with the elimination of water and HCl (56, 57). The development of cationicity is associated with the loss of HCl, since a unit of charge on the polymer is generated for every mole of acid lost, and the pH decreases steadily during the polymerization. In a typical formulation at 12% solids at room temperature, polymerization is complete in $\sim$3 h. The initially colorless solution develops a light blue haze and shows a strong Tyndall effect.

Such a colloidal sol is highly substantive to all papermaking fibers, kraft, sulfite, groundwood, and soda. For its successful use in paper mills, the pH must be kept low, both to prevent precipitation of the resin in an unusable form and to promote curing of the resin; and the concentration of sulfates in the white water on the paper machine must not be allowed to exceed 100 ppm, again because the resin is precipitated in an inactive form by high concentrations of sulfates. High sulfate concentrations may build up in mills using large amounts of alum for setting size or sulfuric acid for controlling pH.

The problem of sulfate sensitivity was solved by adding formaldehyde to the aged colloid that improved wet-strength efficiency and reduced sensitivity to sulfates (58). Later, equivalent results were obtained by adding the extra formaldehyde before the colloid was aged. The additional formaldehyde acts like an acid during the aging process and, unless compensated for by a reduction in the amount of acid charged, lowers the pH to a point where polymerization to the

Table 3. **Formulations for Regular and HE Colloid Resins**

	Regular, MF_3	HE MF_8
water,20° ± 10°C, kg	412.0	330.8
HCl, 20° Bé, kg (1.16 g/mL), kg	17.7	14.1
formaldehyde, 37%, kg		84.8
trimethylolmelamine, kg	45.4	45.4
Total	*475.1*	*475.1*

colloids is inhibited. The high efficiency (HE) resins have been used in mills with sulfate concentrations so high that use of regular trimethylolmelamine (MF_3) colloids would be uneconomical. Sulfate tolerance is a function of the amount of extra formaldehyde present. For best cost-performance, a family of HE colloids is necessary with composition varying from MF_4, for moderate sulfate concentrations, to MF_9, for very high sulfates.

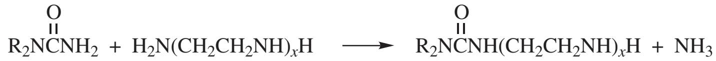
Formulations for regular and HE colloids are shown in Table 3 (59). The materials are added in the order listed to a 454 L (120 gal) tank provided with good agitation and ventilation. Formaldehyde fumes are evolved even from the regular colloid. The colloids develop only after aging and freshly prepared solutions are ineffective for producing wet strength. Stability of the colloids depends on temperature and concentration. Colloids at 10–12% are stable at room temperature for at least 1 week; stability may be extended by dilution after the colloids have aged properly.

Both regular and HE colloids increase the wet strength of paper primarily by increasing adhesion between fibers; the strength of the individual fiber itself is unaffected (60). The resin appears to improve the adhesion between the fibers, whether they are wet or dry, by forming bonds that are unaffected by water. The excess formaldehyde in the HE colloid appears to function by increasing the amount of formaldehyde bound in the colloid (59). The regular colloid, starting with ~3 mol of formaldehyde per 1 mol of melamine, has ~2 mol bound in the colloid and 1 mol free. By mass action, the additional formaldehyde increases the amount of bound formaldehyde in the colloid. When an HE colloid is dialyzed or stored at very low concentrations (0.05%), it loses the extra bound formaldehyde and behaves as a regular colloid.

The first urea–formaldehyde resins used to any extent as wet-strength agents were anionic polymers made by the reaction of a urea resin with sodium bisulfite (61). Attempts to use nonionic urea–formaldehyde polymers were unsuccessful; the neutral charge on the polymer made it unsubstantive to fiber resulting in lack of retention. The sulfomethyl group introduced by reaction with $NaHSO_3$ gave the polymers strong anionicity but substantivity was largely restricted to unbleached kraft pulp. Lignin residues probably provided sites for absorption of the polymer. The use of alum as a mordant was essential, since both the resin and the fiber were anionic. The reaction of bisulfite with the urea–formaldehyde polymer may be represented as

$$R_2N\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2OH + NaHSO_3 \longrightarrow R_2N\overset{\overset{\displaystyle O}{\|}}{C}NHCH_2OSO_2^-Na^+$$

In 1945, cationic urea resins were introduced and quickly supplanted the anionic resins, since they could be used with any type of pulp (62). Although they have now become commodities, their use in the industry has been steadily declining as the shift toward neutral and alkaline papermaking continues. They are commonly made by the reaction of urea and formaldehyde with one or more polyethylene–polyamines. The structure of these resins is very complicated and has not been determined. Ammonia is evolved during the reaction, probably according to the following:



$$R_2N\overset{O}{\overset{\|}{C}}NH_2 + H_2N(CH_2CH_2NH)_xH \longrightarrow R_2N\overset{O}{\overset{\|}{C}}NH(CH_2CH_2NH)_xH + NH_3$$

Formaldehyde may react with the active hydrogens on both the urea and amine groups, and therefore the polymer is probably highly branched. The amount of formaldehyde (2–4 mol per 1 mol urea), the amount and kind of polyamine (10–15%), and resin concentration are variable and hundreds of patents have been issued throughout the world. Generally, the urea, formaldehyde, polyamine, and water react at 80–100°C. The reaction may be carried out in two steps with an initial methylolation at alkaline pH, followed by condensation to the desired degree at acidic pH, or the entire reaction may be carried out under acidic conditions (63). The product is generally a syrup with 25–35% solids and is stable for up to 3 months.

The cationic urea resins are added to paper pulp preferably after all major refining operations have taken place. The pH on the paper machine must be acidic for reasonable rates of cure of the resin. Urea resins do not cure as rapidly as melamine–formaldehyde resins and the wet strength produced is not as resistant to hydrolysis. Furthermore, the resins are not retained as well as the melamine resins. On a resin-retained basis, however, their efficiency is as good. The lower retention of the urea–formaldehyde resins is due to their polydisperse molecular weight distribution. High molecular weight species are strongly absorbed on the fibers and are large enough to bridge two fibers. Low molecular weight species are not retained as well because of fewer charge sites. Attempts to improve the performance of urea–formaldehyde resins by fractionating the syrups by salt or solvent precipitation, or selective freezing or dialysis have been technically successful but economically impractical. The process for production of resins is sufficiently simple so that some paper mills have set up their own production units. With captive production, resins with higher molecular weights and lower stability may be tolerated.

The recovery of fiber from broke (off-specification paper or trim produced in the paper mill) is complicated by high levels of urea–formaldehyde and melamine–formaldehyde wet-strength resin. The urea resins present a lesser problem than the melamine resins because they cure slower and are not as resistant to hydrolysis. Broke from either resin treatment may be reclaimed by hot acidic repulping. Even the melamine resin is hydrolyzed rapidly under acidic conditions at high temperature. The cellulose is far more resistant and is not harmed if the acid is neutralized as soon as repulping is complete.

The TAPPI monograph (64) is an excellent source of additional information on technical and economic aspects of wet strength. An informative overview of the chemistry and mechanisms involved in wet strength chemistry can be found in 65.

Wet-strength applications account for the majority of amino resin sales to the paper industry but substantial volumes are sold for coating applications. The largest use is to improve the resistance of starch-clay coatings to dampness. In offset printing, which is becoming ever more important in the graphic arts, the printing paper is exposed to both ink and water. If the coating lifts from the paper and transfers to the plate, it causes smears and forces a shutdown for cleaning. A wide variety of materials have been added to the coatings to improve wet-rub resistance, including casein, soya protein, poly(vinyl acetate), styrene–butadiene latices, glyoxal–urea resins, and amino resins. Paper coatings are applied at as high a solids content as possible to ease the problem of drying. Retention is not a problem since the resin is applied to a preformed sheet. The important characteristics for coating resins are high solids at low viscosity, high cure rates, and high wet-rub efficiency. Urea and melamine resins or mixtures are sold as high solids syrups or dry powders. They are used with starch-pigment coatings with acidic catalysts, or with starch–pigment–casein (or protein) coatings usually without catalysts. The syrups are frequently methylated for solubility and stability at high solids. All of the resins are of intrinsically low molecular weight to reduce viscosity for ease of handling (see COATINGS, INDUSTRIAL).

Closely allied to resins for treating paper are the resins used to treat regenerated cellulose film (cellophane) that does not have good water resistance unless it is coated with nitrocellulose or poly(vinylidene chloride). Adhesion of the waterproofing coating to the cellophane film is achieved by first treating the cellophane with an amino resin. The cellophane film is passed through a dip tank containing ~1% of a melamine–formaldehyde acid colloid type of resin. Some glycerol may also be present in the resin solution to act as a plasticizer. Resins for this purpose are referred to as anchoring agents.

5.7. Other Uses. Water-soluble melamine–formaldehyde resins are used in the tanning of leather in combination with the usual tanning agents (see LEATHER). By first treating the hides with a melamine–formaldehyde resin, the leather is made more receptive to other tanning agents and the finished product has a lighter color. The amino resin is often referred to as a plumping agent because it makes the finished leather firmer and fuller.

Urea–formaldehyde resins are also used in the manufacture of foams. The resin solution containing an acid catalyst and a surface-active agent is foamed with air and cured. The open-cell type of foam absorbs water readily and is soft enough so that the stems of flowers can be easily processed into it. These features make the urea resin foam ideal for supporting floral displays. Urea–formaldehyde resin may also be foamed in place. A special nozzle brings the resin, catalyst, and foaming agent together. Air pressure is used to deposit the foam where it is desired, eg, within the outside walls of older houses to provide insulation. This application might be expected to grow as energy costs increase, if undesirable odors can be controlled.

Urea–formaldehyde resins are also used as the binder for the sand cores used in the molds for casting hollow metal shapes. The amino resin is mixed with moist sand and formed into the desired shape of the core. After drying and curing, the core is assembled into the mold and the molten metal poured in. Although the cured amino resin is strong enough to hold the core together while the hot metal is solidifying, it decomposes on longer heating. Later, the loose sand may be poured out of the hollow casting and recovered.

6. Regulatory Concerns

Both urea– and melamine–formaldehyde resins are of low toxicity. In the uncured state, the amino resin contains some free formaldehyde that could be objectionable. However, uncured resins have a very unpleasant taste that would discourage ingestion of more than trace amounts. The molded plastic, or the cured resin on textiles or paper may be considered nontoxic. Combustion or thermal decomposition of the cured resins can evolve toxic gases, such as formaldehyde, hydrogen cyanide, and oxides of nitrogen.

Melamine–formaldehyde resins may be used in paper that contacts aqueous and fatty foods according to 21 CFR 121.181.30. However, because a lower PEL has been established by OSHA, some mills are looking for alternatives. Approaches toward achieving lower formaldehyde levels in the resins have been reported (66, 67); the efficacy of these systems needs to be established. Although alternative resins are available, significant changes in the papermaking operation would be required in order for them to be used effectively.

7. Economic Aspects

Japan produces more amino resin than any other country; the United States is next, with the Union of Soviet Socialist Republics, France, the United Kingdom, and Germany following.

Many large chemical companies produce amino resins and the raw materials needed, ie, formaldehyde, urea, and melamine. Some companies may buy raw materials to produce amino resins for use in their own products, such as plywood, chipboard, paper, textiles, or paints, and may also find it profitable to market these resins to smaller companies. The technology is highly developed and sales must be supported by adequate technical service to select the correct resin and see that it is applied under the best conditions.

During the past 10 years there has been considerable change in the suppliers of amino resins as a result of acquisitions, spin-offs and withdrawal of some of the smaller companies from the business. The following is a representative list of those currently in the business:

> Badische Aniline and Soda-Fabrik (BASF), Ludwigshafen, Germany; Berger International Chemicals, Newcastle upon Tyne, England; Borden Chemical Div., Columbus, OH; Casella Farbwerk Mainkur A.G., Frankfurt-Fechenheim, Germany; Cuyahoga Plastics, Cleveland, OH; Cytec Industries, West Patterson, NJ; DSM Coating Resins, Zwolle, Holland; Dainippon Ink, Ltd., Tokyo, Japan; Dynamit-Nobel, A.G., Troisdorf-Koln, Germany; Fiberite Corp, Winona, MN; Georgia-Pacific Corp., Atlanta, GA; Gulf Adhesives, Lansdale,

PA; Hitachi Chemical Co. Ltd, Tokyo, Japan; Matsushita Electric Works, Ltd., Osaka, Japan; McWhorter Technologies, Carpentersville, IL (Division of Eastman Chemical Co., Kingsport, TN); Melamine Chemicals, Donaldson, LA (Division of Borden Chemical, Columbus, OH); Mitsui-Toatsu Chemicals, Ltd, Tokyo, Japan; Mitsui-Cytec, Ltd., Tokyo, Japan; Montedison SpA, Milan, Italy; Pacific Resins, Tacoma, WA; Perstorp AB, Perstorp, Sweden; Perstorp Compounds, Inc., Florence, MA; Reichhold Chemicals, White Plains, NY (Division of Dainippon Ink, Tokyo, Japan); Solutia, Inc, St. Louis, MO; Sumitomo Ltd., Tokyo, Japan; Vianova Resins GmbH & Co. Wiesbaden, Germany (Division of Solutia, St. Louis, MO).

BIBLIOGRAPHY

"Amino Resins and Plastics" in *ECT* 1st ed., Vol. 1, pp. 741–771, by P. O. Powers, Battelle Memorial Institute; in "Amino Resins and Plastics" *ECT* 2nd ed., Vol. 2, pp. 225–258, by H. P. Wohnsiedler, American Cyanamid Company; in "Amino Resins and Plastics" *ECT* 3rd ed., Vol. 2, pp. 440–469, by I. H. Updegraff, S. T. Moore, W. F. Herbes, and P. B. Roth, American Cyanamid Company; *ECT* 4th ed., Vol. 2, pp. 604–637, by Laurence L. Williams, American Cyanamid Company; " Amino Resins and Plastics" in *ECT* (online), posting date: December 4, 2000, by Laurence L. Williams, American Cyanamid Company.

CITED PUBLICATIONS

1. R. Bainbridge, *Sail* **8**(1), 142 (1977).
2. A. Einhorn and A. Hamburger, *Ber. Dtsch. Chem. Ges.* **41**, 24 (1908).
3. Brit. Pats. 248,477 (Dec. 5, 1924), 258,950 (July 1, 1925), 266,028 (Nov. 5, 1925), E. C. Rossiter (to British Cyanides Company, Ltd.).
4. Brit. Pats. 187,605 (Oct. 17, 1922), 202,651 (Aug. 17, 1923), 208,761 (Sept. 20, 1922), H. Goldschmidt and O. Neuss.
5. Brit. Pats. 171,096 (Nov. 1, 1921), 181,014 (May 20, 1922), 193,420 (Feb. 17, 1923), 201,906 (July 23, 1923), 206,512 (July 23, 1923), 213,567 (Mar. 31, 1923), 238,904 (Aug. 25, 1924), 270,840 (Oct. 1, 1924), 248,729 (Mar. 3, 1925), F. Pollak.
6. U.S. Pat. 1,460,606 (July 3, 1923), K. Ripper.
7. Ger. Pat. 647,303 (July 6, 1937), Brit. Pat. 455,008 (Oct. 12, 1936), W. Hentrich and R. Köhler (to Henkel and Co., GmbH).
8. R. Rager, *Mod. Plast.* **49**(4), 67 (1972).
9. E. Drechsel, *J. Prakt. Chem.* [2] **13**, 330 (1876).
10. U.S. Pat. 2,727,037 (Dec. 13, 1955), C. A. Hochwalt (to Monsanto Chemical Company).
11. Ger. Pat. 1,812,120 (June 11, 1970), D. Fromm, K. W. Leonhard, R. Mohr, M. Schwartzmann, and H. Woehrle (to Badische Anilin und Soda-Fabrik A.G.).
12. P. Ellwood, *Chem. Eng.* **77**(23), 101 (1970).
13. J. F. Walker, *Formaldehyde, American Chemical Society Monograph, No. 159,* 3rd ed., Reinhold Publishing Corp., New York, 1964.
14. *U.F. Concentrate-85,* Technical Bulletin, Allied Chemical Corp., New York, 1985.
15. U.S. Pat. 3,129,226 (Apr. 14, 1964), G. K. Cleek and A. Sadle (to Allied Chemical Corp.).
16. U.S. Pat. 3,458,464 (July 29, 1969), D. S. Shriver and E. J. Bara (to Allied Chemical Corp.).

17. Ref. 13, p. 151.
18. *N-(iso-butoxymethyl) acrylamide, Technical Bulletin PRC 126,* American Cyanamid Co., Wayne, N.J., Feb. 1976.
19. M. Gordon, A. Halliwell, and T. Wilson, *J. Appl. Polym. Sci.* **10**, 1153 (1966).
20. J. W. Aldersley, M. Gordon, A. Halliwell, and T. Wilson, *Polymer* **9**, 345 (1968).
21. I. H. Anderson, M. Cawley, and W. Steedman, *Br. Polym. J.* **1**, 24 (1969).
22. K. Sato, *Bull. Chem. Soc. Jpn.* **40**(4), 724 (1967) (in Eng.).
23. K. Sato and T. Naito, *Polym. J.* **5**, 144 (1973).
24. K. Sato and Y. Abe, *J. Polym. Sci. Polym. Chem. Ed.* **13**, 263 (1975).
25. V. A. Shenai and J. M. Manjeshwar, *J. Appl. Polym. Sci.* **18**, 1407 (1974).
26. A. Berge, S. Gudmundsen, and J. Ugelstad, *Eur. Polym. J.* **5**, 171 (1969).
27. A. Berge, B. Kvaeven, and J. Ugelstad, *Eur. Polym. J.* **6**, 981 (1970).
28. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.* **71**, 643, 661, 890 (1952); **72**, 88, 139, 202, 207, 213, 1027 (1953).
29. R. Steele, *J. Appl. Polym. Sci.* **4**, 45 (1960).
30. G. A. Crowe and C. C. Lynch, *J. Am. Chem. Soc.* **70**, 3795 (1948); **71**, 3731 (1949); **72**, 3622 (1950).
31. Brit. Pat. 829,953 (Mar. 9, 1960), E. Elbel.
32. U.S. Pats. 3,007,885 (Nov. 7, 1961), 3,114,930 (Dec. 24, 1963), W. N. Oldham, N. A. Granito, and B. Kerfoot (to American Cyanamid Co.).
33. U.S. Pat. 3,661,819 (May 9, 1972), J. N. Koral and M. Petschel, Jr. (to American Cyanamid Co.).
34. U.S. Pat. 3,803,095 (Apr. 9, 1974), L. J. Calbo and J. N. Koral (to American Cyanamid Co.).
35. W. Lindlaw, *The Preparation of Butylated Urea–Formaldehyde and Butylated Melamine Formaldehyde Resins Using Celanese Formcel and Celanese Paraformaldehyde,* Technical Bulletin, Celanese Chemical Co., New York, Table XIIA.
36. *Technical Bulletin S-23-8,* 1967, *Supplement to Technical Bulletin S-23-8,* 1968, Celanese Chemical Co., Example VIII.
37. W. J. Blank and W. L. Hensley, *J. Paint Technol.* **46**, 46 (1974).
38. U.S. Pat. 2,517,750 (Aug. 8, 1950), A. L. Wilson (to Union Carbide and Carbon Corp.).
39. U.S. Pat. 2,304,624 (Dec. 8, 1942), W. J. Burke (to E. I. du Pont de Nemours & Co., Inc.).
40. U.S. Pat. 3,324,062 (June 6, 1967), G. S. Y. Poon (to Dan River Mills Inc.).
41. H. Kadowaki, *Bull. Chem. Soc. Jpn.* **11**, 248 (1936).
42. U.S. Pat. 3,089,859 (May 14, 1963), T. Oshima (to Sumitomo Chemical Company, Ltd.).
43. U.S. Pats. 2,731,472 (Jan. 17, 1956), 2,764,573 (Sept. 25, 1956), Bruno V. Reibnitz and co-workers (to Badische Anilin-und Soda-Fabrik); U.S. Pat. 2,876,062 (Mar. 3, 1959), Erich Torke (to Phrix-Werke A.G.).
44. U.S. Pat. 3,487,088 (Dec. 30, 1969), K. H. Remley (to American Cyanamid Co.).
45. U.S. Pat. 3,524,876 (Aug. 18, 1970), J. E. Gregson (to Dan River Mills, Inc.).
46. U.S. Pat. 3,658,458 (Apr. 25, 1972), D. J. Gale (to Deering Milliken Research Corp.).
47. U.S. Pats. 2,602,017; 2,602,018 (July 1, 1952), L. Beer.
48. C. Hasegawa, *J. Soc. Chem. Ind. Jpn.* **45**, 416 (1942).
49. U.S. Pat. 3,212,955 (Oct. 19, 1965), S. Kaizerman (to American Cyanamid Co.).
50. U.S. Pat. 4,741,804 (May 3, 1988), D. B. Solarek and co-workers (to National Starch and Chemical Corp.).
51. U.S. Pat. 4,605,702 (Aug. 12, 1986), G. J. Guerro, R. J. Proverb, and R. F. Tarvin (to American Cyanamid Co.).
52. U.S. Pats. 2,926,116; 2,926,154 (Feb. 23, 1960); G. L. Keim (to Hercules Powder Co.).
53. U.S. Pat. 2,345,543 (Mar. 28, 1944), H. P. Wohnsiedler and W. M. Thomas (to American Cyanamid Co.).

54. C. G. Landes and C. S. Maxwell, *Pap. Trade J.* **121**(6), 37 (1945).
55. Ger. Pat. 2,332,046 (Jan. 23, 1975), W. Guender and G. Reuss (to Badische Anilin- und Soda-Fabrik A.G.).
56. J. K. Dixon, G. L. M. Christopher, and D. J. Salley, *Pap. Trade J.* **127**(20), 49 (1948).
57. Unpublished data, American Cyanamid Co.
58. U.S. Pat. 2,559,220 (July 3, 1951), C. S. Maxwell and C. G. Landes (to American Cyanamid Co.).
59. C. S. Maxwell and R. R. House, *TAPPI* **44**(5), 370 (1961).
60. D. J. Salley and A. F. Blockman, *Pap. Trade J.* **121**(6), 41 (1945).
61. U.S. Pat. 2,407,599 (Sept. 10, 1946), R. W. Auten and J. L. Rainey (to Resinous Products and Chemical Co.).
62. U.S. Pat. 2,742,450 (Apr. 17, 1956), R. S. Yost and R. W. Auten (to Rohm and Haas Co.).
63. U.S. Pat. 2,683,134 (July 6, 1954), J. B. Davidson and E. J. Romatowski (to Allied Chemical and Dye Corp.).
64. J. P. Weidner, ed., *Wet Strength in Paper and Paper Board, Monograph Series, No. 29,* Technical Association of Pulp and Paper Industry, New York, 1965.
65. K. W. Britt in J. P. Casey, ed., *Pulp and Paper,* Vol. III, John Wiley & Sons, Inc., New York, 1981, Chapt. 18.
66. W. Kamutzki, *Ind. Carta* **26**(6), 297 (1988).
67. W. Kamutzki, *Kunstharz-Nachr.* **24**, 9 (1987).

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