

Aminoplastics

By C. P. VALE, M.A., A.R.I.C.

*Research Chemist,
British Industrial Plastics Ltd.*

THE AMINO RESINS are a group of synthetics which continue to find new applications in many industrial fields, and there is thus a great need for this concise monograph on their characteristics and uses.

The making of such diverse products as glues, lacquers, enamels, textiles, plywood, printing inks, electrical components and certain types of paper has been much influenced by the great potentialities of these substances, although to the general public they are most familiar in domestic and fancy ware, for which the gay colours they will take render them very suitable.

After a short account of the chemistry and formation of the urea-formaldehyde, the melamine and allied resins, the author describes the uses of moulding powders, the properties and testing of mouldings, and the use of aminoplastics for lacquers, adhesives, textiles, paper and other special purposes. There are full references to more detailed sources of information.

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C. P. VALE

M.A., A.R.I.C.

*Research Chemist, British Industrial Plastics Ltd.
Late Exhibitioner of St. Catharine's College, Cambridge.*

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To my Wife

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PREFACE

IN this work an attempt has been made to collate the technical literature relating to the chemistry of the amino resins and to survey their use and applications in various industries.

Hitherto, the abundant literature dealing with these resins and their uses has remained scattered, while general text-books of plastics, which cover a variety of materials, usually give scant attention to this particular field and in certain cases the information given is somewhat ill-balanced.

It is hoped that this book will not only prove useful as a work of reference to those engaged within the aminoplastics industry and to lecturers, students and apprentices, but also be of value to those engaged in the plywood, textile, paper and other industries which the amino resins serve.

I should like here to express my thanks to Mr. A. Brookes, M.B.E. (Research Manager, B.I.P.), for his encouragement and most valued criticism and advice throughout the preparation of this book.

I also owe a considerable debt of gratitude to my friend, Mr. James Moore, for much help with the diagrams and proofs, and to Miss Vera Haigh for preparing an excellent typescript.

Finally, I would like to thank my colleagues on the Research Staff of B.I.P. who have helped me in one way or another with advice and criticism, and the Chairman and Directors of B.I.P. for permission to publish.

Smethwick
May 1950

C. P. VALE

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INTRODUCTION

SYNTHETIC resinous products which are formed by the interaction of an aldehyde (usually formaldehyde) and a compound containing more than one amino ($-\text{NH}_2$) group per molecule are now well known by the generic name of aminoplasts. Compounds which have been found to give commercially useful resins include urea ($\text{CO}(\text{NH}_2)_2$), melamine ($\text{C}_3\text{N}_3(\text{NH}_2)_3$) and to a lesser extent thiourea ($\text{CS}(\text{NH}_2)_2$), and guanidine ($\text{HN}:\text{C}(\text{NH}_2)_2$). Strictly these compounds are not amines, but belong to the class of organic substances known as the amides. They react chemically with formaldehyde to give, under mild conditions, methylol derivatives (i.e., compounds containing the group $-\text{CH}_2\text{OH}$) which on heating are converted irreversibly, by progressive condensation, to hard, colourless, transparent resins.

Certain true amines such as aniline ($\text{C}_6\text{H}_5\text{NH}_2$) do react with formaldehyde to give commercially useful resinous products, but in these cases the process of resinification is fundamentally different. The products have different properties and although technically these too are aminoplastics, they are excluded from consideration in this book.

The primary non-resinous reaction products of urea and formaldehyde were isolated and studied as early as 1884, but it was not until a patent was published in 1918 by John, describing the formation of resins, that commercial possibilities were envisaged. The earliest work on these resins was directed almost exclusively to attempts to produce an organic substitute for glass.

From about 1924, however, attention was turned to the possibility of producing moulding compositions capable of conversion to useful moulded articles by the hot-pressing technique, already fully established for phenolic resin compositions. The first successful amino resin based moulding composition of this type was introduced in Great Britain in 1926, and was based on a mixed urea-thiourea formaldehyde condensate. In due course high grade moulding powders based on urea-formaldehyde resin alone were successfully developed.

Urea resins were also manufactured, initially in Germany by the I.G. Farbenindustrie, for use as plywood adhesives, and "Kaurit" cements began to appear commercially in 1936. Research, carried out mainly in Great Britain, eventually led to the production of urea adhesives successfully modified so as to be used for general constructional purposes.

Other uses for urea resins which have been developed have included their application as media for the production of synthetic stoving and air-drying enamels; as materials suitable for imparting crease-resistance and other advantageous properties to cellulose and protein fabrics; and, in more recent years, as agents for the production of paper possessing high wet strength.

In all these developments full advantage has been taken of the colourless and light-fast nature of the resins, properties in which aminoplastics are superior to the phenolics. The advent of materials which possess these properties combined with the greater heat-resistance and water-resistance of the phenolics, came about in 1935 with the discovery of melamine-formaldehyde resins.

Melamine, also known as cyanuramide, melts at a much higher temperature than urea and is considerably less soluble in water. These facts may account for the

superior heat and water-resistance of melamine resins.

Until quite recently, melamine was a rare and expensive chemical. The commercial possibilities of melamine resins have resulted in the development of numerous processes designed to give melamine in good yield at relatively low cost. Though still more expensive than urea, the advantages to be gained in the use of melamine resins have in many cases outweighed the disadvantage of higher cost, and the resins are becoming of increasing commercial importance.

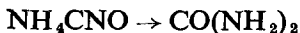
CHAPTER I

UREA-FORMALDEHYDE RESINS

THE chemical reactions that take place between urea and formaldehyde, giving rise to resinous products, form an important aspect of the study of aminoplastics. Before considering the nature of these reactions, it is relevant to describe the methods of manufacture and properties of the two starting materials. The growing demand for both urea and formaldehyde over the past forty years has led to important developments resulting in their manufacture from readily available raw materials at comparatively low cost.

UREA

Urea (or carbamide) derives its name from the fact that it occurs in urine to the extent of about 3 per cent. It was first obtained from that source in 1773, and prepared artificially for the first time by Wöhler¹ in 1828 by the isomeric transformation of ammonium cyanate upon evaporation of a solution to dryness:

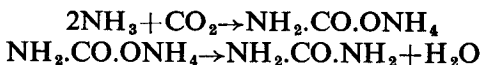


On a commercial scale, developments in the methods of production were undertaken from 1920 onwards, more particularly by the Badische Anilin und Soda Fabrik Gesellschaft in Germany, and by 1925 manufacturing processes based on many of these improvements were well established.

Urea is usually prepared on a large scale by causing

liquid carbon dioxide and liquid ammonia to react together at elevated temperatures and pressures in steel autoclaves lined with silver or lead to withstand the highly corrosive action of the liquid mixture.

Ammonium carbamate, which is first formed, decomposes to give urea and water as follows:

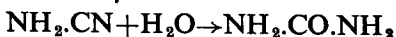


The mixture of urea and unchanged ammonium carbamate is taken up in water, and the carbamate decomposed by heat to give ammonia and carbon dioxide which are then recycled to the compressors. The urea is isolated from the solution by vacuum evaporation or spray drying.

Differing techniques have been suggested in numerous papers and patents. Yakovkin,³ saturating liquid carbon dioxide with ammonia, and employing pressures of 75–80 atmospheres and temperatures of 160–170°C. obtained a 40 per cent conversion. Krase, Clark and Gaddy⁴ using 100–110 atmospheres and 153°C., recorded yields of 35–37 per cent. Bolotov and Popova⁵ obtained yields of 50–60 per cent by employing 10–15 per cent excess ammonia, pressures of 150–175 atmospheres and temperatures of 175–185°C.

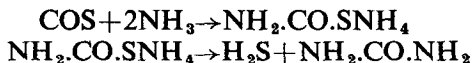
Other methods which have been suggested for the manufacture of urea include:

(a) the hydrolysis of cyanamide⁶ (see page 48) in concentrated aqueous solution with small quantities of sulphuric acid at 60°C.,



(b) the interaction of liquid ammonia and liquid carbon

oxysulphide in stainless steel autoclaves at 80–120°C. under pressures which increase to 18 atmospheres owing to the liberation of hydrogen sulphide,



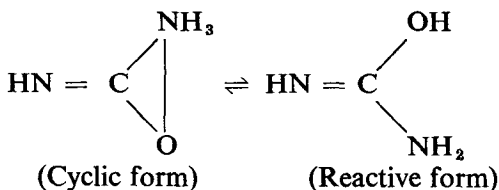
Yields of 70–80 per cent have been claimed using this method.⁷

Urea is a white crystalline solid melting at 132.6°C. It dissolves readily in water (105 grams per 100 at 20°C., 246 grams per 100 at 60°C., 725 grams per 100 at 100°C.), less readily in ethyl alcohol (5.4 grams per 100 at 20°C., 15.1 grams per 100 at 60°C.) and is almost insoluble in diethyl ether (0.0004 gram per 100 at 20°C.). On heating it decomposes above the melting point with the liberation of ammonia, leaving a residue which contains cyanuric acid ($\text{C}_3\text{H}_3\text{O}_3\text{N}_3$) and biuret ($\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$). An alkaline solution of the residue when treated with one drop of aqueous copper sulphate gives a violet or pink colouration. This colouration is given by biuret, and in general by all compounds containing two $-\text{CO}\cdot\text{NH}-$ groups either combined together, or joined to the same nitrogen or carbon atom.

Urea behaves as a very weak mono-acid base, and forms salts with a number of acids. Urea nitrate $\text{CO}(\text{NH}_2)_2\cdot\text{HNO}_3$ and urea oxalate $[\text{CO}(\text{NH}_2)_2]_2\cdot\text{C}_2\text{H}_2\text{O}_4$, for example, may readily be precipitated by adding the appropriate acid, in concentrated solution, to a concentrated aqueous solution of urea.

The commonly accepted structure for urea is $\text{NH}_2\cdot\text{CO}\cdot\text{NH}_2$ and for elementary considerations of the properties of the compound this formula suffices. As a result of considerable investigations on the properties

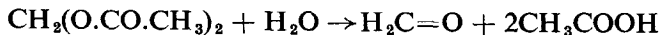
of urea and its derivatives, however, Werner⁸ came to the conclusion that, in aqueous solution, urea behaves as an equilibrium mixture of the two forms:



the presence of acids tending to favour the formation of the reactive form.

FORMALDEHYDE

This compound is the first member of the homologous series of aliphatic aldehydes. It was first obtained by Butlerow⁹ in 1859, who hydrolyzed methylene acetate in an attempt to synthesize methylene glycol:



It was prepared in 1868 by Hofmann,¹⁰ who passed a mixture of methyl alcohol vapour and air over a heated platinum wire.

Formaldehyde is a gas which condenses on chilling to give a liquid boiling at -19°C . It has an unpleasant odour, and its vapours are highly irritating to the eyes, nose and upper respiratory tracts. Formaldehyde is almost invariably sold, transported and used either in aqueous solution, or in a solid polymeric state.

The manufacture of formaldehyde was probably started by the firm of Mercklin and Lösekann in Germany in 1889. Other concerns took up the manufacture in the eighteen-nineties, commercial production extending to the U.S.A. in 1901.

The principal method of manufacture involves the catalytic oxidation of methanol vapour. When a mixture of methanol vapour and air is passed over a heated copper gauze, for example, formaldehyde is obtained, probably by a process of dehydrogenation:

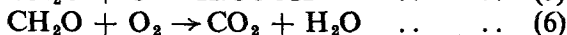
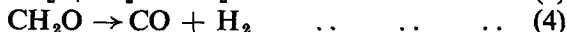


The reaction was originally believed to be one of simple oxidation:



but mechanism studies have shown that the reaction represented by equation (2) probably takes place to only a small extent, if at all.

Further reactions which occur during the process are as follows:



In practice the conditions are arranged so that the reactions represented by equations (4), (5) and (7) are made as feeble as possible. Temperatures in the region of 500°C. are employed, and the products are passed through scrubbers and coolers. A solution of formaldehyde, containing methanol and small quantities of formic acid, is thus obtained. In older plants this solution was fractionally distilled to recover some of the unchanged methanol. Later improvements in technique have tended to eliminate this procedure, and modern