

Technical Section

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PLAINTIFF'S EXHIBIT

UC-5284

Advances in plastics during 1940

General*

ATREND of vast purport has been toward the utilization of plastics by the armed forces of every major nation.^{1,2} Military applications, definite and potential, include laminated materials in airplane construction, cast resins in guide lines on airplane carriers, luminescent resins in various military devices, tinted cellulose acetate windows for air raid protection, gun stocks of cellulose acetate and fabric-filled phenolic resins, cellulose acetate chutes for conveying ammunition belts from boxes to machine guns in airplanes, phenolic mouthpieces and containers for gas masks, impregnation of the fabric of gas masks with vinyl chloride resin as a protection against mustard gas, cellulose acetate in soldier's goggles, phenolic noses of anti-aircraft shells, and the possible application of Nylon as a parachute material. In three British fighting services the uses of synthetic resins are said to exceed 1000 in number. A survey of plastics in the United States defense economy indicated that all types were amply available and that the molding and laminating plants were capable of handling extensive increases in production demands.³

Another item of general interest is the recommendation in British regulations for the electrical equipment of buildings that electrical apparatus of the all-insulated type be installed wherever practicable and that the use of electrical apparatus (particularly electric toasters and hairdryers) having exposed metal parts be avoided as far as possible. Lamp-holders so constructed of, or so shrouded in, insulating material that it is impossible to touch any metal part were also recommended. The availability of plastics for the construction of all-insulated equipment, particularly molded housings, is said to have prompted this action.⁴

Materials

No really new plastics appeared on the market during 1940, but outstanding progress in developing increased volume and new markets can be credited especially to the vinyl ester resins and cellulose acetate butyrate. These materials took many of the awards in the Fifth Annual Modern Plastics Competition.⁵ Vinylidene

chloride resin is commanding attention in its applications as high-strength fibers and seat coverings. Nylon resin is entering the industrial field as brushes for brushes used in the textile printing trade.⁶ Other highlights of the year in materials development include the production of plastics from cellulose acetate of lower acetyl content (58 percent acetic acid) than previously employed,⁸ and the further activity in the manufacturing of melamine resin.⁹ Investigations pertaining to the use of farm waste products for the production of plastics were reported on by the Agricultural By-Products Laboratory, Ames, Iowa,¹⁰ and by the University of Tennessee Research Corporation.¹¹

Molding and fabricating

Improvements in injection and compression molding presses have been concerned primarily with various operating features, particularly heating¹² and automatic controls.¹³ The technique of continuously extruding thermoplastic materials has also advanced considerably during the past year¹⁴ and extruded plastics are replacing reed and rattan in woven furniture.¹⁵ A process for forming molds by spraying metal against a model has been perfected to the point where production molds have been made and are being tested in service.¹⁶

Applications

The aircraft industry has, of course, been spotlighted during the past year and further important strides were made in the use of plastic plywood for molding airplane wings and fuselages.¹⁷ An outstanding development in this field was the laminated plastic tab for use on aileron, elevators and rudders to aid in balancing and controlling the airplane during flight.¹⁸ The reinforced plastic contributes a saving in weight and greater rigidity in this part. Many new applications of plastic

* Prepared by G. M. Kline for inclusion in the annual report of the Sub-Division on Rubber and Plastics of the American Society of Mechanical Engineers, Dec. 5, 1940, New York.

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Melamine resins impart easy sanding qualities to clear wood lacquers and sealers

fore, found use in a wide variety of metal enamels. Special urea-alkyd resin combinations were also developed during 1940 which for certain applications, such as clear wood finishes, could be baked at temperatures much lower than required by previously available thermosetting resins. As the answer to production line requirements, they will certainly find increased use in the near future. Plasticized urea resins in emulsion form also found use in considerable volume during 1940 as clear finishes on paper and textiles.

(c) *Melamine resins.*—Undoubtedly the most outstanding development for the paint industry in 1940 was the commercial production of organic soluble resins made from melamine. Like those made from urea, they are thermosetting types which find their major application in baking enamels in conjunction with alkyd resins. When such combinations are baked at the temperature range normally used for urea types, they bake more quickly and to a degree of hardness which is quite extraordinary, closely approaching molded plastics in this respect. Melamine resins have also been found more generally suitable than the urea types for relatively low baking schedules and they retain gloss and color to a much greater degree on prolonged subjection to high heats. They also exhibit superior resistance to weather exposure and to grease and chemicals. With this combination of characteristics melamine resins are going into enamels for use on everything from stoves to refrigerators, from autos to cake boxes.

Baking equipment

In the ordinary baking oven, heat transfer is accomplished by convection air currents. Improved ventilating devices have assured not only more uniform heating throughout the oven but better heat transfer by eliminating the blanketing of the work by a layer of solvent vapor and dead air. During the past year there has developed a more widespread use of other methods of heating such as electrical induction and, more particularly, the use of infrared lamps.

The pioneer work by the Ford Motor Company on baking of undercoats on automobile bodies with infrared lamps has been watched with ever-growing interest by other users of industrial finishes. There now seems to be a better realization of the efficiency of this means

of focusing heat on a finished surface. It frequently means the ability to bake at a substantially higher temperature than is feasible when the whole mass of the finished article has to be heated up in the event. Furthermore, the newer resins, particularly the urea and melamine types, have been found especially suitable for these quick high-temperature bakes and have contributed largely to development of this technique.

Future developments

A review of the recent past readily justifies the keen anticipation with which the paint industry is facing the future. The manufacture of surface coatings has definitely passed into the hands of technical experts and rich rewards await those who are alert to take prompt advantage of the continued stream of developments from the many research laboratories in their own and the chemical industry.

Phenol resins

by S. H. HALL*

UNFORTUNATELY for a discussion of this type the record of progress made during the past year in phenolic resins is confined to the few theoretical investigations which have appeared in print and the patents allowed. Research on the phenol-aldehyde types which was most extensive during the previous years is not revealed strongly in either the reports of theoretical search or patents. However, there is no doubt that there is a tremendous amount of research in this field by manufacturers, and evidence of their progress is constantly revealed by improved physical characteristics in their molding compounds. Obviously, most of the work along this line is not available except in so far as the few patents granted.

Further evidence to substantiate claims that ether bridges are formed as a primary reaction in the resinification of dimethylol phenols is offered in "The Hardening of Phenol-Formaldehyde Resins." In "The Chemical Nature of Phenol-Aldehyde Resins" the author covers several aspects of primary reactions, resinification reactions and reactions to the final C stage. A picture of the physical structure of phenol-aldehyde resin by P. M. Kozloy² reveals it as a colloidal system with the solid high molecular polymer as the disperse phase and a mutually soluble mixture of phenol-alcohol derivative of dihydroxydiphenylmethane and water as the plastic-solvent phase, the catalyst acting as a stabilizer. It explains hardening and other changes in mechanical properties by this hypothesis. Still another theory from the physical standpoint is found in "Phenol Plastics."³ The formation of methylene bridges is concluded in "General Formaldehyde Resin Mechanism." Evidence of similar dielectric behavior in five phenol-formaldehyde condensation products is revealed in a study of "The Electrical Properties of Thermoplastics."⁴

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The trend of industrial research from a survey of the patents allowed is shown definitely to be primarily along modified lines which comprise by far the largest group. Very little appears in the strictly unmodified group. The most interesting developments in this latter group are the cold-setting of a liquid phenol-formaldehyde resin with acid,⁷ a water soluble phenol-aldehyde condensation product with an alkaline catalyst which is suitable for blending with latex,⁸ and a liquid resin composition which will not harden at room temperature but will harden relatively rapidly at elevated temperatures.⁹

Turning to the modified group, one finds several excellent advances in resins for coatings and impregnating varnishes.¹⁰⁻¹⁴ Apparently researchers are gradually bridging the gap between the brittle phenolic molded pieces and the more elastic rubber pieces, and when the final span has been laid another tremendous upswing in the phenolic plastics field may be expected. A product has been obtained by reacting rubber, maleic anhydride and a phenol at elevated temperature plus a further reacting with an aldehyde, which is suitable for molding compositions.¹⁵ Replacement of hexa with dimethylol urea improves the color of phenol-formaldehyde resins.¹⁶ A glass-clear, transparent condensation product is obtained by reacting phenol with formaldehyde with an alkaline catalyst, lactic acid and a reactive urea-formaldehyde condensation product.¹⁷ Of interest, also, is a liquid resin suitable for casting which cures in two to three days at 70-80 deg. C.¹⁸ A resin suitable for coatings, adhesives, fabric impregnation, brake linings and molding compositions is made from a resin-like phenol-aldehyde reacted with an ester from esterifying cashew nut shell liquid.¹⁹ A phenol-formaldehyde resin, formaldehyde-hardened soybean meal and woodflour in the proportions of 3:3:2 is said to produce a molding compound with as fine a finish, cure, strength and permanence as the average phenolic compound.²⁰ Yet another material for molding, coatings or creaseproof fabrics has been patented—formed by reacting a phenol, an aromatic sulfonamid and a halogenated aliphatic group.²¹

There has been also a great expansion or broadening of research in pursuit of further applications as witnessed by the tremendous increase in the development of phenolic resins for varnishes, enamels, printing inks and other important outlets.²²⁻⁴⁶ Conclusive proof of advancement is no doubt revealed in the consistent increase of production by the phenolic-resin manufacturers, such production being indisputable evidence of new and greater service being rendered industry in general.

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Reservoirs overhead and resin kettles below are used for blending phenol, formaldehyde and catalysts.

