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VARIABLY CURING RESINS FOR
MOUNTING METALLOGRAPHIC SAMPLES

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VARIABLY CURING RESINS FOR MOUNTING METALLOGRAPHIC SAMPLES

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ABSTRACT

In the past, heat-and-pressure-curing resins have been used almost exclusively as mounting materials for metallographic samples. Now, however, certain polyester resins, which are curable at room temperature, are equally as good for this purpose, and with their versatility they adapt readily to a variety of mounting conditions.

A study of the epoxies and polyesters was made to determine which type of resin would satisfy the desirable properties of a metallographic mount. Four polyester resins were selected and investigated intensively to ascertain the variables associated with their curing processes. The results are compared with the standard thermosetting mounting material, Bakelite.

INTRODUCTION

Early in the 1950's research in plastics had developed improved products which could compete with other materials. Until this time most of the uses of plastics were directed toward war-time applications. There is little wonder, then, why the heat-and-pressure-curing phenolic resins, which appeared commercially in 1909 and are exceeded in age among the synthetic plastics only by cellulose nitrate, were chosen as the best materials for mounting metallographic specimens.^(1,2) Room-temperature curing resins have been described by Everhart⁽³⁾ and by Kehl and Church,⁽⁴⁾ but their rather complex mixing procedure and the relatively poor properties of the materials obtained limited use to situations in which the heat and pressure needed for the thermosetting process to cure the phenolic resins would have caused a phase transformation or deformation of the specimen. Recently, N. Gendron⁽⁵⁾ has reported the use of resins cured at room temperature as a standard mounting practice in the General Electric Laboratories. Although these resins still left many properties to be desired in a mounting material, their use was justified in comparison with the heat-and-pressure-curing phenolic Bakelite.* Cramer and Schonfeld⁽⁶⁾ reported

*Product of Union Carbide and Carbon Corp., New York, New York.

the use of a room-temperature-curing resin as a standard mounting material for toxic metals which are handled in gloveboxes in which it is difficult to use a mounting press. The development of resins which can compete with Bakelite as materials for mounting of metallographic specimens is the result of rapid advances in the field of plastics during the last few years. Their use will undoubtedly increase in the future. This report is intended to familiarize the metallurgist with the types of room-temperature-curing resins available and their capabilities in relation to their use as metallographic mounting materials. Emphasis is on four resins which can be used to solve most mounting problems. The authors fully recognize that research and development in this field will result in new products which may be superior for this application but the principles contained herein should remain unchanged.

TYPES OF RESINS

Resins are classified into two main groups as thermoplastic and thermosetting. The thermoplastic resins soften when heated and return to their initial condition when cooled to room temperature. They are usually composed of linear polymers and are known as nonconvertible materials. The thermosetting resins are converted into an infusible and relatively insoluble condition by heat, and do not soften appreciably when reheated. The film structure of these resins is composed of cross-linked molecules or polymers. They are referred to as heat-convertible resins.

Typical thermoplastic resins are the styrene polymers and copolymers, acryls, celluloses, polyethylenes, vinyls and polyvinyls, polyamides, acetals, and the various fluorocarbons. The thermosetting resins are the alkyds, polyesters, epoxies, aminos (melamine and ureas), and phenolics. The reader is referred to the book by the Manufacturing Chemists Association⁽⁷⁾ for examples of the above resins, their manufacturers, and their typical properties.

Resins to be useful as mounting materials must be cured to a hard mass. Hardening of a resin, whether it is thermoplastic or thermosetting, is accomplished by controlling complex chemical reactions. The normal result of the chemical reaction is a polymerization or linking of molecular structure together.

In general, the chemical reaction may be initiated by one or a combination of curing systems. The systems generally considered are heat, heat and pressure, catalysts (the catalyst initiates an exothermic chemical reaction), ultraviolet light, and nuclear radiation. Since the thermoplastic resins will soften when heated, they are usually handled commercially as solids (powder, flake, or solid pieces) which have been cured by one of the first three methods. They are then reworked or shaped by the application

of heat or of heat and pressure. The thermosetting resins which do not soften appreciably on heating after curing are usually handled commercially as liquids. They are composed of polymers which are not cross-linked, i. e., they are still in the thermoplastic stage. On further curing, these resins change to a hard infusible mass by cross-linking.

DESIRABLE PROPERTIES OF A METALLOGRAPHIC MOUNTING MATERIAL

In order to select a resin for metallographic mounting we must first define the properties that are desirable in this application. These properties are described below:

1. Sufficient hardness - a beveled surface is more easily prevented and specimen edges are preserved when the mounting material is hard. A hard mounting material is desirable when hand grinding hard metallographic specimens so that the mount does not wear away and leave the specimen as a pivot point. The hardness of Bakelite is R_M 100-108; therefore, the hardness of a competitive mounting material should be in or above this range.
2. Low curing temperature - the standard mounting material, Bakelite, requires a heat-and-pressure system for curing. The use of pressure lowers the temperature necessary for curing and also insures good contact of the Bakelite with the specimen. Curing temperatures up to 150°C, the curing temperature of Bakelite, should probably be considered as acceptable. The curing temperature should be kept as low as possible and the pressure eliminated to reduce the possibility of incurring a phase transformation in the specimen during mounting.
3. Adhesion to all types of specimens - good adhesion is necessary in order to preserve the edges of a specimen during the polishing operation. Openings around the specimen entrap grit and polish when the surface is being prepared. These entrapped particles, which are difficult to remove, may be pulled out during a final polishing operation, causing scratches on the polished surface of the specimen. It is very difficult to prevent staining of a polished surface if there are voids around the specimen where etching reagents and cleaning solutions can be entrapped. Also, a tapered sample might fall out of the mount if the resin has poor adhesion properties.
4. No voids when cast - voids are not usually a problem in the normal mounting operations because the average specimen does not contain small crevices which are difficult to fill with resin. If this problem arises, then the resin must have the ability to fill in the voids, or the problems mentioned in (3) will be encountered. Bubbles formed in some

liquid resins can be eliminated to some extent by pulling a vacuum on the resin or applying pressure before curing. These techniques are undesirable because they introduce another step in the curing process.

5. Good chemical resistance to the common solvents and etching reagents - since Bakelite and Lucite have fair resistance to these chemicals, any resin being considered as a mounting material should have equivalent or better chemical resistance.

6. Short curing time - a curing time of several minutes is desirable for any mounting material regardless of its method of cure, but equally important is the ability to mount many samples at the same time. It is precisely this ability that makes the resins which use a catalyst system for curing attractive as materials for mounting metallographic samples. The total curing time with catalyst systems is usually much longer than the 15 min required for Bakelite mounting, but the only limit to the number of samples that can be mounted at one time is the amount of resin that can be mixed and poured before the resin hardens.

7. Simple preparation - in comparison with the method of preparing the thermosetting phenolic Bakelite, by means of the heat-and-pressure-curing system, the methods of preparing resins by the catalyst systems of curing are equally as simple, provided the right resin systems are used. Resins which require special equipment or techniques for curing, such as pressure, drying, curing in a vacuum, and refrigeration during curing, should be avoided, because these operations only complicate the curing process.

8. Adequate toughness - the mount must be able to withstand the mechanical shock of dropping on a hard surface.

9. Transparent - a resin should be sufficiently transparent for the specimen to be seen through the mount.

10. High heat-distortion temperature - the resin must not soften and flow during grinding. This problem would cause smearing of the specimen surface with resin and gumming of the grinding paper.

11. Safe to handle - to be competitive with heat-and-pressure curing a resin-catalyst system must not propose a danger to the personnel who will be associated with its use. The pungent odor associated with some of the resins was not considered a limitation because they can be used in a well-ventilated room or a hood.

COMPARISON OF RESIN SYSTEMS

The selection of a resin for a particular application is an extremely difficult task, even for the experienced worker. Most manufacturers develop

their resins with the intention of supplying the consumer with a variety of products which have various specific properties depending on the demands of the consumer. The problem of selecting a suitable metallographic mounting resin is enhanced because the available literature contains only spotty information; additional testing is left to the user. Also, the changes in properties associated with an alteration of the surrounding conditions are not well defined and must usually be decided by experiment for each resin and catalyst system. Nevertheless, the choices from a variety of potential mounting resins can be reduced substantially by eliminating those resins which have undesirable properties.

The thermoplastic resins have, in general, a lower optimum hardness than many of the thermosetting resins. The former usually require the undesirable heat-and-pressure-curing system to obtain maximum properties (good chemical resistance and high hardness). Therefore, all of the thermoplastic resins as well as the thermosetting resins which require heat-and-pressure-curing systems can be eliminated as potential mounting materials. On the basis of the considerations mentioned above, two groups of thermosetting resins are particularly attractive: the polyesters and epoxies.

Each of the many manufacturers of polyester resins possesses several basic resin formulations which in themselves have various modifications. In contrast with the polyesters, the epoxy resins are manufactured by a relatively small group of firms which have only a few basic formulations. Modifications of both types of resins are made by slight changes in formulation of the raw materials, by blending, or by the use of additives.

When two manufacturers specify the same value in a specific property, the resins may differ extremely in many of their other properties. The various manufacturers have their own formulations for a specific property, and, since many ingredients go into a resin, the final product has a high probability of being nowhere near the same composition of another manufacturer's resin. Blending of resins is sometimes highly successful in producing desired properties.

Some of the properties which make the polyesters of interest are low cost, high hardness, rapid curing, controlled curing, and apparent non-toxicity.⁽⁸⁾ Their properties are usually not sensitive to slight variations in catalyst additions and the polyesters have good chemical resistance.⁽⁹⁾ They hold a specimen with a gripping action that is caused by shrinkage of the resin on curing.

The epoxies may be rapidly cured. They have a high hardness, excellent chemical resistance, and a relatively high cost.⁽¹⁰⁾ Their properties are usually sensitive to slight variations in catalyst additions. The catalysts which develop maximum properties in the epoxy resins are

toxic.⁽¹¹⁾ Some of the uncured epoxy resins are considered somewhat irritating to the skin, but the amine hardeners are mostly responsible for ailments. The most common allergies are eczema, system poisoning, asthma attacks, and general irritation of the skin. The best measures to prevent ailments are good housekeeping and careful work habits, along with adequate ventilation to draw the fumes away from the worker. These hardeners are to be avoided in mounting of metallographic samples because the precautions necessary for their handling seriously limit their usefulness.

The cured epoxies are usually nondeleterious to health. In all fairness, the toxicity of catalysts has been a problem to the industry. As a result, new low-toxicity catalysts were developed;⁽¹²⁾ however, their use is still somewhat limited when maximum properties are desired.

The epoxies have the unique property of partially bonding to the specimen. This could be a problem if the specimen must be removed from the mount. In comparison with the polyesters and epoxies the phenolic resins are inexpensive, have a high hardness and good chemical resistance.

The above statements concerning the properties of resins are general statements covering many resin formulations. The specific properties of the individual resins may deviate significantly from the general properties. There are other properties of resins which are associated with the curing systems. These properties can only be compared after a more thorough discussion of the curing process.

CURING OF POLYESTER AND EPOXY RESINS

Several terms which may help to understand the curing of polyester and epoxy resins are defined below:

1. Catalyst: That chemical which induces the conversion of the liquid resin to a solid infusible condition. It may also be called a hardener or an initiator.

2. Inhibitor: A chemical which is added to polyester resins to suppress the curing process in the resins at room temperature.

3. Promotor: A chemical which is added to a resin to insure a controlled cure. When the catalyst is added to a resin it reacts with the promotor, producing an exothermic chemical reaction which supplies the heat needed for curing.

4. Accelerator: Another chemical which can be added to a resin to obtain an even more rapid reaction with the catalyst and a faster cure, if desired. The terms accelerator and promotor are sometimes used interchangeably.

5. Pot Life: The time from the addition of the catalyst to the solidification of the resin. These resins solidify (gel) a short time before the exothermic chemical reaction is observed.

6. Exotherm: The amount of heat given off during curing; usually defined as the maximum temperature rise of a quantity of resin.

7. Post Curing: Holding incompletely cured resin which is in the gelled state at a temperature slightly above room temperature for a length of time necessary to give complete curing of the resin and thus to obtain its optimum properties. This technique can be used effectively where the user wishes to cure a resin to its optimum properties without going through the high exotherm necessary to cure the resin completely in one step.

From these definitions the general curing of a liquid resin-catalyst system can now be described. A small amount of promotor is added to the polyester resin. An accelerator can be added at this time if desired. Many resins are commercially available with the promotor and accelerator already added. After a thorough mixing, the catalyst is then added to the resin (polyester or epoxy) and mixing is continued. The resin is then poured into a mold and allowed to harden. After a period of time, the resin gels and an exothermic chemical reaction takes place. When the resin has cooled to room temperature it is removed from the mold. The pot life, the exotherm, and the physical properties of a particular resin are dependent on the quantity and type of catalyst, promotor, accelerator if used, and the molding conditions. It can easily be seen that with this number of variables these resins are extremely flexible and adapt readily to many molding processes.

Use of the catalyst in an amount which is considered much greater than optimum for a certain resin could result in an extremely rapid cure, causing a fire. Certain additives can be explosive if mixed together; therefore, only responsible personnel should handle these materials. A general rule for additives, which will be discussed later, is to do all mixing in the resin. The authors do not wish to instill fear in the personnel required to handle these materials, but rather to stress the shortcomings of experimenting with chemicals which are unfamiliar.

PRELIMINARY TESTING

Elimination of many of the resin formulations because of their undesirable properties was made by a study of the literature and technical bulletins. A preliminary test was then conducted with some of the remaining resins to determine their capabilities. Catalyst and promotor additions (methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline) were made to the resins according to manufacturers' recommendations or were determined by experiment when instructions were lacking. Lists of the

resins, their manufacturers, and the catalyst system used with each resin are given in Tables I, II, and III.

Table I

POLYESTER RESINS USED IN THE PRELIMINARY TESTS

Manufacturer	Resin Designation*
Reichhold Chemicals Inc RCI Building White Plains, New York	Polylite 523
	" 8027
	" 8063
	" 8173
Hooker Electrochemical Co Durez Plastics Division North Tonawanda, New York	Hetron 72
	" 92
	" 197
Allied Chemical Company Plastics & Coal Chemicals Div 40 Rector Street New York 6 New York	Plaskon 9500
	" 9600
	PE-13
	PE-125
	PE-153
	PE-155
	PE-169
PE-228	
PE-236	
U S Rubber Company Naugatuck Chemical Division Naugatuck, Connecticut	Vibrin 154
American Cyanamid Company Plastics & Resins Division 30 Rockefeller Plaza New York 20, New York	Laminac 4107
	" 4111

All polyesters were cured with the methyl ethyl ketone peroxide catalyst. Cobalt naphthenate solution and dimethylalanine were added when needed.

Table II

EPOXY RESINS AND CURING AGENTS USED IN THE PRELIMINARY TESTS

Manufacturer	Resin Designation	Curing Agents
Reichhold Chemicals, Inc RCI Building White Plains, New York	Epituf 6130	2605
	" 6140	2605
	" 6131	2605
	"	A
	"	D
	"	Z
	"	T-1 TETRA
Ciba Company Inc Plastics Division Kimberlon, Pennsylvania	Aralorte 6010	Versamid 125
Union Carbide Corporation Bakelite Company Plastics Div 30 East 42nd Street New York 17, New York	ERL 2795	2605
	"	A
	"	D
	"	Z
	"	T-1
	"	TETRA
	"	ZZL-0814
Shell Chemical Company 380 Madison Avenue New York 17, New York	Epon 828	2605
	"	A
	"	D
	"	Z
	"	T-1
	"	TETRA
	"	ZZL-0814

Table III

MANUFACTURERS AND TYPES OF CURING AGENTS USED WITH THE EPOXY RESINS

Manufacturer	Curing Agent	Type
Reichhold Chemicals Inc RCI Building White Plains, New York	2605	
General Mills, Inc Chemical Division Kankakee, Illinois	Versamid 125	Polyamide
Shell Chemical Company 380 Madison Avenue New York 17, New York	A	Diethylamino-propylamine
	D	Tri (2-ethyl hexoate) salt of tri (dimethyl amino methyl) phenol
	Z	Eutectic mixture of modified aromatic amines
	T-1	Modified aliphatic amine
	TETA	Triethylene tetra amine
Bakelite Company Division of Union Carbide Corp 30 East 42nd Street New York 17, New York	ZZL-0814	Aliphatic Amine-ethylene Oxide Adduct

The mixed resins were cast in polyethylene cups, 1-in. in diameter. The ends of the casting were machined until flat and parallel, and the Rockwell "M" hardness was measured on a Kentrall hardness tester according to procedure A of ASTM Test No. D785-60T.⁽¹³⁾ The castings were then post cured and the hardness again measured. In this way the highest hardness of a resin was determined without experimenting to find the exact amount of catalyst necessary to obtain its optimum properties in the normal one-step method of curing. The amount of bubbles, clarity, and ease of mixing were also observed. During testing, some resins were formulated as many as six times to obtain

samples with the optimum properties of a certain resin-catalyst system. Some of the castings were full of bubbles and could not be used for accurate hardness measurements. From these preliminary results it was obvious that many resin-catalyst systems could be used for mounting metallographic samples; however, their development into usable systems for this purpose could only be achieved by a thorough investigation of the casting variables. Therefore, extensive testing was unavoidable. To simplify this investigation, several of the most promising resin-catalyst systems were selected and their properties were studied intensively. The resins selected for complete testing were PE-169, PE-228, Poly-lite 8063 and Polylite 8173. These resins are all polyesters.

CHEMISTRY OF POLYESTER RESINS

To familiarize the metallurgist with the basic chemical reactions that take place when polyesters are cured, we have included an abridged discussion of the ingredients and their purposes. A more complete discussion of the chemistry of polyester resins can be found in the books by Bjorksten Research Laboratories⁽⁸⁾ and Lawrence.⁽¹⁴⁾

In organic chemistry the reaction of an organic acid with an organic base is called an esterification or condensation reaction, and the products are an ester and water. An example is the combination of monobasic acetic acid and monohydric ethyl alcohol to form a simple ester, ethyl acetate, and water. In Figure 1 the reaction is shown in terms of the reactive groups of each molecule. Longer or more complex molecules called polymers (poly - many; mer - unit) can be formed from a polybasic acid and a polyhydric alcohol as shown in Figure 2. Unsaturated polyesters which are capable of thermosetting (cross-linking) are made from unsaturated dibasic acids and glycols. This reaction, involving both saturated and unsaturated acids, is illustrated in Figure 3. The polyesters are unique in their formulation. They are compounded from one or more of three or four dibasic acids and from one or more of as many glycols at necessary proportions. The principal dibasic acids used are phthalic and maleic anhydrides, fumaric, isophthalic, and adipic acids. The glycols are ethylene, propylene, diethylene, and dipropylene. The polyesters produced are linear in structure with recurring double bonds. Unsaturated polyesters cure by: (1) additional polymerization among themselves, (2) by additional polymerization through cross-linkage with unsaturated monomers, usually styrene, or with any other unsaturated copolymerizable monomers through the reactive double bonds of the cross-linking agent and the double bonds of the ethylene glycol maleate chain. This reaction is shown in Figure 4 with the before-and-after cure configurations. The monomers usually used are thin liquids, and they serve as solvents for the normally viscous polyesters. The monomers in general are styrene, diallyl phthalate, and triallyl cyanurate. Styrene is the least expensive and the one most commonly used in resins. The monomers may be used by themselves or in varying proportions with one another to attain desirable properties.

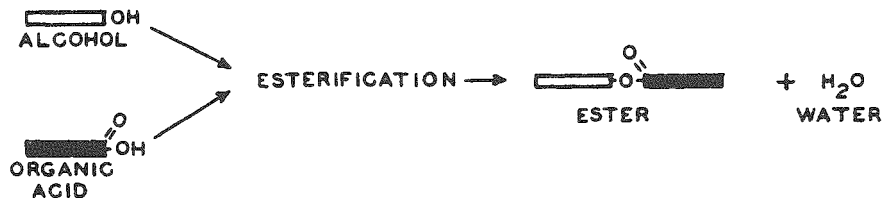


Fig. 1. Simple Esterification Reaction of a Monobasic Acid with a Monohydric Alcohol. (Courtesy Reinhold Publishing Corporation⁽¹⁴⁾)

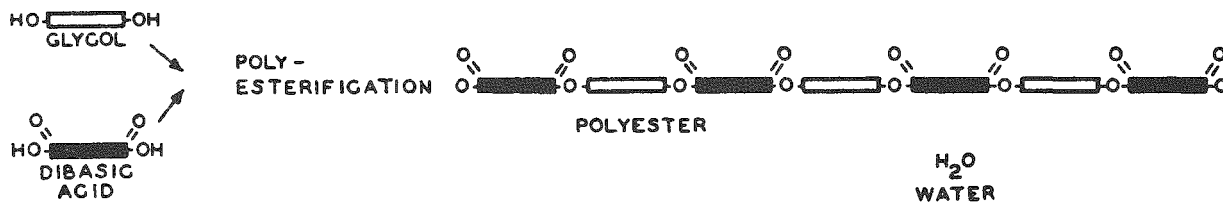


Fig. 2. Polyesterification Reaction of a Polybasic Acid with a Polyhydric Alcohol. (Courtesy Reinhold Publishing Corporation⁽¹⁴⁾)

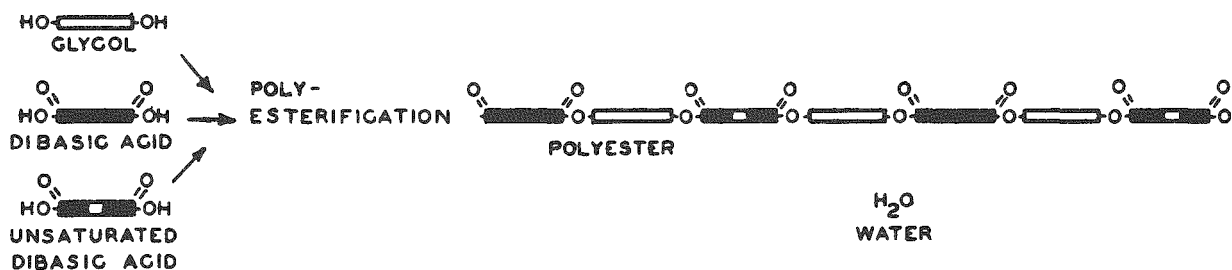


Fig. 3. Polyesterification Reaction Involving Both Saturated and Unsaturated Acids. (Courtesy Reinhold Publishing Corporation⁽¹⁴⁾)

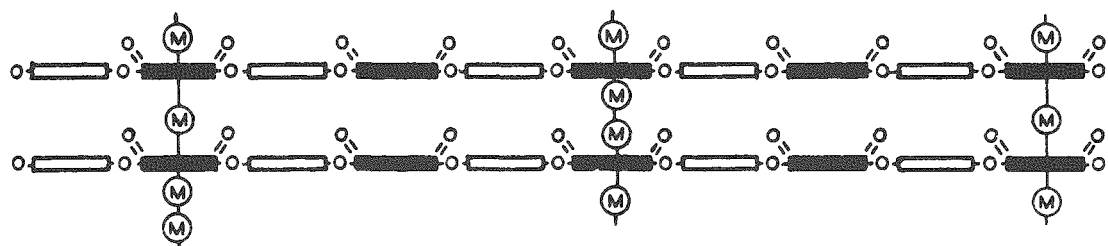
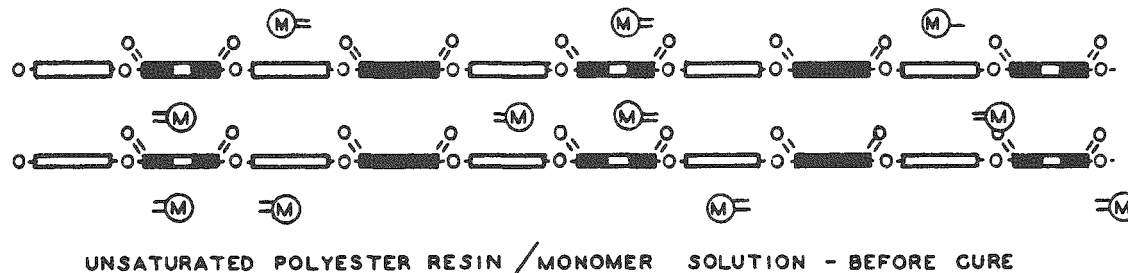


Fig. 4. Polyester/Monomer Mixture before and after Cure. (Courtesy Reinhold Publishing Corporation⁽¹⁴⁾)

The shelf life of a polyester resin is limited since polymerization is continually taking place at a very slow rate between the monomer and the polyester. To increase the storage time an inhibitor is added to the resins to slow down or temporarily arrest this reaction. Two principal types of inhibitors have been developed for polyester resins. One type is called a "retardant." Its inhibiting effects are independent of temperature and directly proportional to their concentration in the resin. A frequently used retardant is hydroquinone. The inhibitors of the other type are called "stabilizers." Some of the compounds most generally associated with this group are salts of the substituted hydrazines, quaternary ammonia salts, and substituted parabenzquinones.⁽⁸⁾ The action of the stabilizers is to stabilize the resin mix at room temperature and yet permit fast and complete cure at higher temperatures. Even with the inhibitor, the shelf life of polyesters is restricted to room temperature and may be from several months to a year, depending upon the resin system and type and amount of inhibitor. The polyester resins are very sensitive to ultra-violet light. Therefore, they must be protected from this light in order to prevent premature gelling of the resin. Resins stored in tightly sealed metal containers seem to have the longest shelf life.

Promoters (accelerators) are added to the resins to speed the decomposition of the catalyst into free radicals - a process which is normally slow and uncontrolled at room temperature. Cobalt naphthenate solution* (6% cobalt) is very effective as a promotor which continues the curing reaction in catalyst systems which cure from room temperature. A double-promotor system may be used when the curing time must be accelerated without the addition of an increased amount of catalyst or when maximum properties are needed rapidly. In such a case one promotor develops rapid gel formation and the other acts to complete the cure. An example of such a system would be cobalt naphthenate, dimethyl-aniline,* with methyl ethyl ketone peroxide* as the catalyst.**

Cross-linking of a polyester resin is initiated by the catalyst, which decomposes and forms free radicals. The free radicals open the carbon atom double bonds by sharing electrons with one of the carbon atoms. Since two electrons are released when the double bonds open, the other electron stays with the partner carbon atom. The partner atom is then free to behave like a free radical capable of opening and adding to other double bonds in the monomer or polymer (see Figure 4). Decomposition of the catalyst is accelerated by heat with a half-life from minutes to many hours. The organic peroxides are the usual chemicals associated with the catalytic effects on polyesters.⁽¹⁵⁾

*Obtainable from most distributors of plastics supplies. The chemicals used in the experiments described in this report were purchased from Cadillac Plastics and Chemical Co., Chicago, Illinois, or from Lucidol Division, Wallace and Tiernan, Inc., Buffalo, New York.

**Promoters are never to be mixed directly with the catalyst because an explosion would occur. They must be thoroughly mixed with the resin before the catalyst is added.

Cure of a polyester resin may be accomplished by time. If the resin is allowed to set beyond its shelf life, some cross-linking of the polyester chains with the monomer will take place. This very slow process can be speeded by the use of ultraviolet light, heat, or nuclear radiation. Rapid and controlled cure can only be obtained with the use of catalyst systems. There are room-temperature catalyst systems, just-above-room-temperature systems, and others which must be heated to 100°C or more before they will initiate polymerization. The room-temperature catalyst systems are the most desirable for mounting of metallographic specimens because, in general, the lowest curing temperatures are provided. The choice of a room-temperature cure essentially limits the selection of the catalyst to methyl ethyl ketone peroxide and of the promotor to cobalt naphthenate. Although other catalyst-promotor systems could probably be employed by those skilled in the art to accomplish some of the objectives stated above, this system is the simplest and easiest to use. The catalyst methyl ethyl ketone peroxide (MEKP) when used by itself will usually cure a polyester resin after several hours in an uncontrolled manner with a low exotherm. The resin must then be post-cured at a temperature of about 100°C for an hour to attain its maximum physical properties. Additions of small amounts of promotor produce curing in a controlled period of time with a controlled temperature rise. The normal practice is to use a determined value for the amount of promotor and to vary the catalyst content. This gives good control of pot life and exotherm. In general, the catalyst content should never be dropped below 0.5 w/o or full cure cannot be attained. The use of too much catalyst will produce a very rapid reaction with the promotor, and the resulting high exotherm from the cross-linking reaction could destroy the casting.

The normal cure of a liquid polyester resin takes place through autoacceleration. After addition of the catalyst, initial cross-linking takes place, forming a gel structure which decreases the mobility of the system. This restricted state causes a decrease in the frequency of termination reactions (growing chains) and an increase in the number of addition reactions to other double bonds. More heat is liberated in the latter reaction and the heat, in turn, speeds the release of more radicals from the decomposing catalyst which accelerates the addition reactions. The system automatically heats very rapidly as its mobility decreases. The rapid increase in temperature of the resin mass during this change from the gel to the cured state can set up strains in the casting, causing cracking and brittleness. The degree of exotherm is a measure of the activity and unsaturation of the resin. An increase in the promotor or catalyst causes a decrease in curing time and an increase in the exotherm. Heat added to most catalyst systems will accelerate the curing reaction, causing an increase in the exotherm. When the walls of the container are well insulated and the quantity of resin is about 100 g, the temperature of the mass can rise very rapidly to 230°C or more. When the internal heating is low and heat is lost at a rapid rate to the surroundings or to the mold itself, the resin may not attain its

maximum properties and post-curing will be necessary for complete polymerization. Problems caused by the exothermic nature of the cure can be avoided by the proper selection of the resin and careful use of the catalyst and promotor.

EXPERIMENTAL

Four resins, Polylyte 8063, Polylyte 8173, PE-169, and PE-228, were mixed with various percentages by weight of methyl ethyl ketone peroxide (MEKP). Polyester 169 and PE-228 are manufactured as double-promoted systems with one of the promotors being cobalt naphthenate solution. Both Polylyte resins are clear but 8173 has a pink cast. Polyesters 169 and 228 are dark in color. A specimen mounted in either of the latter two resins can be seen if its mount is held in front of a light.

The amount of MEKP and cobalt naphthenate solution (6% cobalt) required was usually of the order of a per cent. Accurate and easy weighing of the hardener and cobalt solution was done by determining the number of drops from a standard dropper in one gram and then adding the number of drops corresponding to the calculated weight percentage of addition to the resin. Cobalt naphthenate solution was mixed into Polylyte 8063 before the hardener was added. These additions were kept to within one drop (± 0.03 w/o) of the required amount of 2 or 4 w/o.

Several materials were considered as containers, stirring rods, and molds for casting these resins. Polyethylene cups and stirring rods were selected for mixing because the liquid resin was easily cleaned off with tissue wet with acetone. Paper cups also made excellent mixing containers and they were discarded after use, since their cost was nominal.

The best method of handling the resin was to store it in tightly sealed, one-quart metal containers. When a container was opened the resin in it was completely used up before a new container was opened. By this method of storage only a small portion of the resin was exposed to the light and air when castings were made and this resin was used up quickly.

Three molds, each one inch in inside diameter, (see Figure 5) were selected to investigate the effect of mold material and mold thickness on the curing of the resins. One mold was a polyethylene sleeve $\frac{1}{16}$ in. thick, with a tightly fitting cover (see Figure 5a). This mold melted slightly and could not be reused if the exotherm of the resin rose above about 100°C. Identical thin-walled molds were later machined from stock Teflon for use at the higher exotherms. Another mold with a thick wall (see Figure 5b) was also machined from stock Teflon to measure the effect of a heat sink around the casting. The casting surface of the Teflon molds were carefully prepared so as not to contain any ridges which could cause the cured casting to stick to the mold wall.

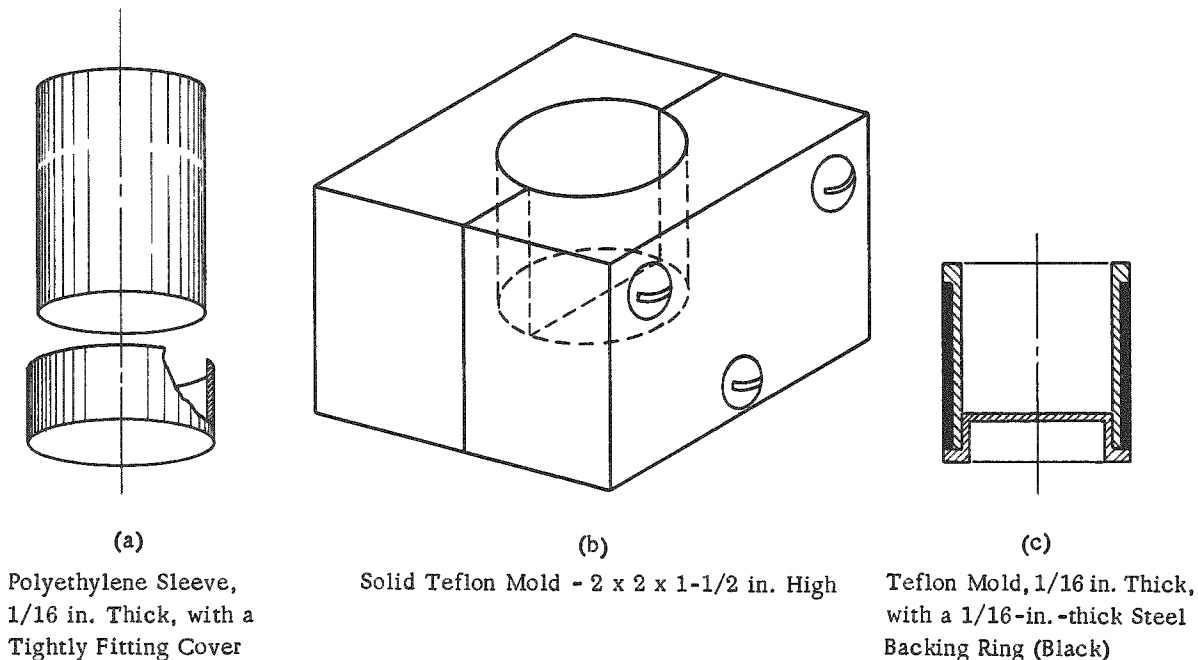


Fig. 5. Various Molds That Were Used to Make 1-in.-diameter by $\frac{3}{4}$ -in.-high Castings of Polyester Resins.

Resin was poured to a height of about $\frac{3}{4}$ in. in the mold. A chromel-alumel thermocouple was placed in the center of the resin, and the temperature was recorded as a function of time on a Leeds and Northrup multipoint strip-chart recorder. The values of pot life and exotherm were determined from the chart record. The pot life was taken as the period of time from mixing of the catalyst in the resin to a rise in temperature. This value was probably greater than the true pot life because gelling of the resin usually preceded the exotherm by several minutes, especially when the pot life was long.

The ends of the castings were ground on SiC paper to a depth of about $\frac{1}{16}$ in. and the R_M hardness⁽¹³⁾ was measured as previously described. The reported hardness value is the average of three or more readings taken randomly on the ends of each casting. Some of the incompletely cured castings were then post cured in a laboratory oven at temperatures of 60, 70, and 80°C for various times and the hardness was remeasured.

The back of the as-cast mounts became very sticky when certain solvents, such as trichlorethylene or carbon tetrachloride, came into contact with this surface. This chemical attack was attributed to a high concentration of the unreacted styrene formed there because it rises during the curing process. The layer of softened resin was easily removed by wiping this surface with a tissue soaked with acetone or by grinding.

RESULTS

Representative curves of temperature versus time after addition of the catalyst, taken from the strip chart recorder, are plotted in Figures 6a, b, c, and d for each resin. The temperature rose to a higher value in a shorter time as the percentage of MEKP was increased. The values apply only to the molding conditions described previously; changes in the mold material, thickness of the mold, diameter of the casting, or quantity of resin might change these curves. These curves are useful in predicting the total curing time of a resin for a particular addition of hardener.

Curves showing changes in properties of the various resins as a function of their MEKP content can be seen in Figures 7 through 11. They have about the same general shapes. All of the curves presented here are for fresh resin, that is, resin which has not been stored beyond its shelf life. These curves may shift and possibly change shape if the resin is old. The old resin can be cured, but curing may not proceed in a controlled manner as it does with fresh resin.

Pot lives, plotted as a function of the percentage MEKP added to the resins, are shown in Figure 7 a-d. Pot life time decreased rapidly and then leveled off as the percentage of MEKP was increased. Points from the curves of Figure 7 a-d were plotted on log-log scales in Figure 8. For all of the resins, except Polylyte 8173 with additions of MEKP above 3.5 w/o, a linear relationship was obtained between the pot life and per cent MEKP additions. Values for the equation

$$y = cx^n$$

where

$$y = \text{pot life (min)} \quad ; \quad x = \text{w/o MEKP} \quad ; \quad c = \text{constant} \quad ,$$

were determined from the line for each resin. These equations are given in Table IV. The change in slope of the line for Polylyte 8173 with more than 3.5 w/o MEKP indicates that a limiting process is active above this value. The straight-line relationship between the pot life and per cent MEKP when plotted on the log-log scales shows how accurately the curing process is controlled with respect to pot life and irrespective of the mold material or mold thickness.

The effect of increasing amounts of MEKP on the exotherm is shown in Figure 9 a-d for the thin- and thick-walled molds. Although the exotherm increased as the percentage of MEKP was increased, there appeared to be a range of rapid increase and then a more gradual increase or a possible leveling off. The thick-walled mold of Figure 5b apparently extracted more

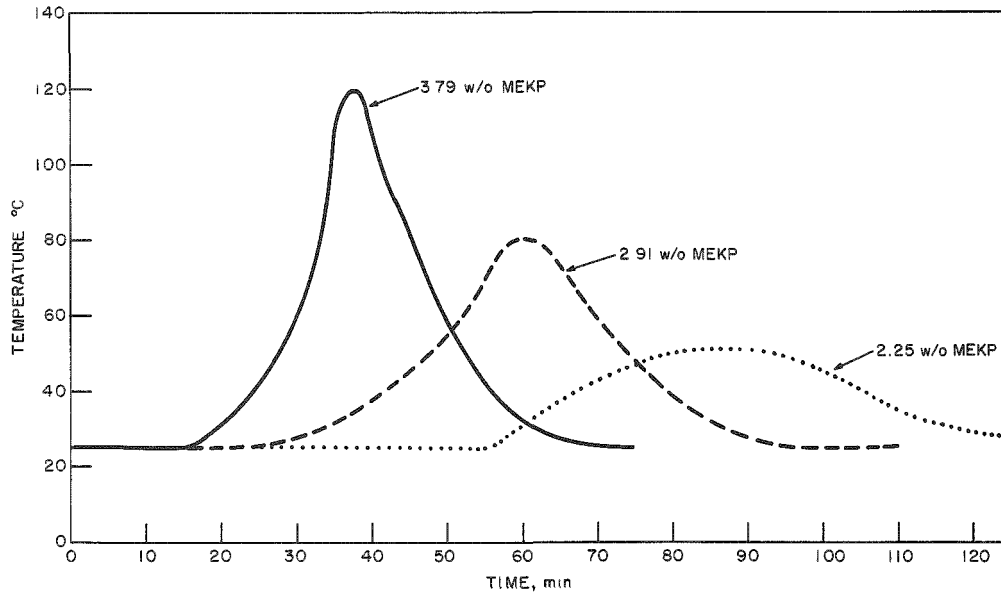


Fig. 6a. Representative Curves of Temperature versus Time after Addition of Catalyst for Polylite 8173 in a Thin-walled Mold.

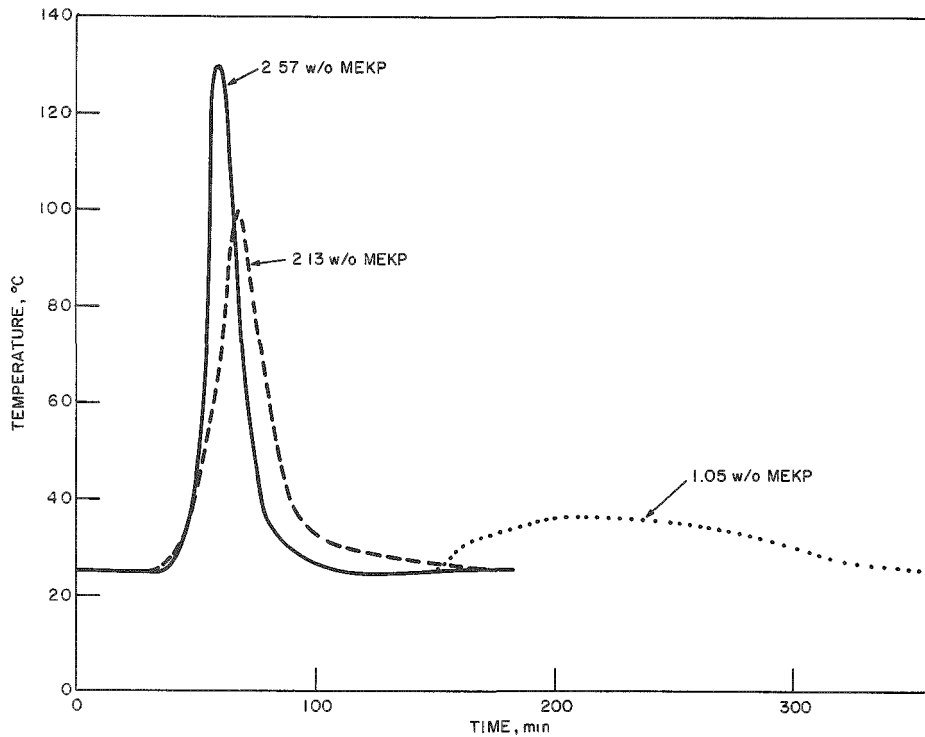


Fig. 6b. Representative Curves of Temperature versus Time after Addition of Catalyst for Polylite 8063, with 0.4 w/o Co and Use of a Thin-walled Mold.

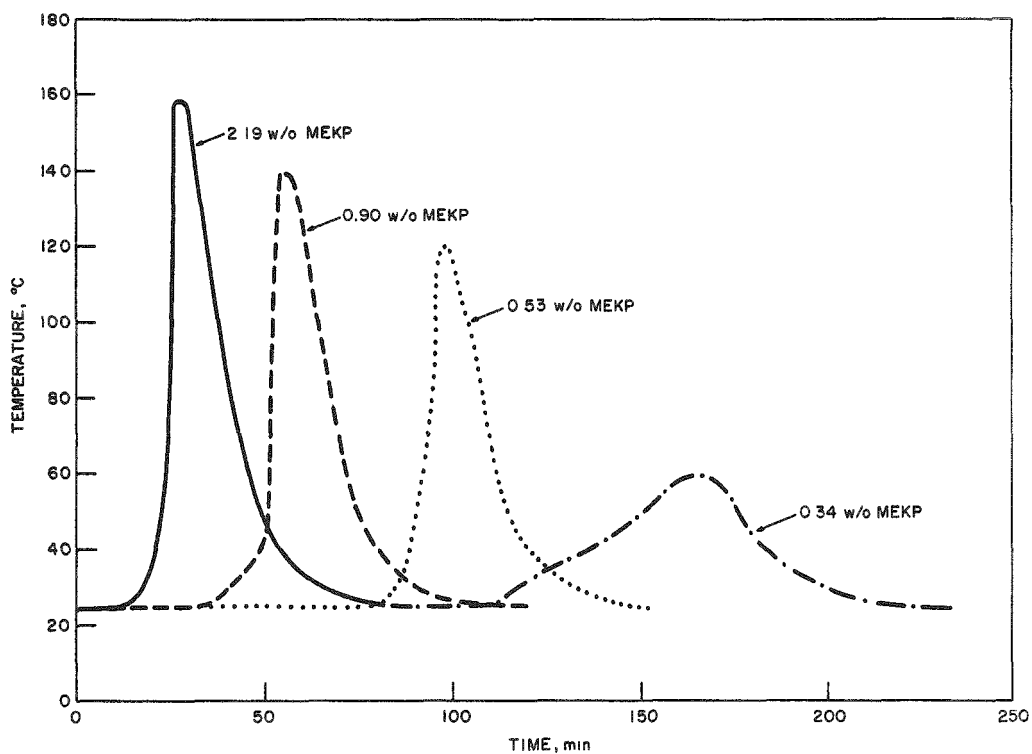


Fig. 6c. Representative Curves of Temperature versus Time after Addition of Catalyst for PE-169 in a Thin-walled Mold.

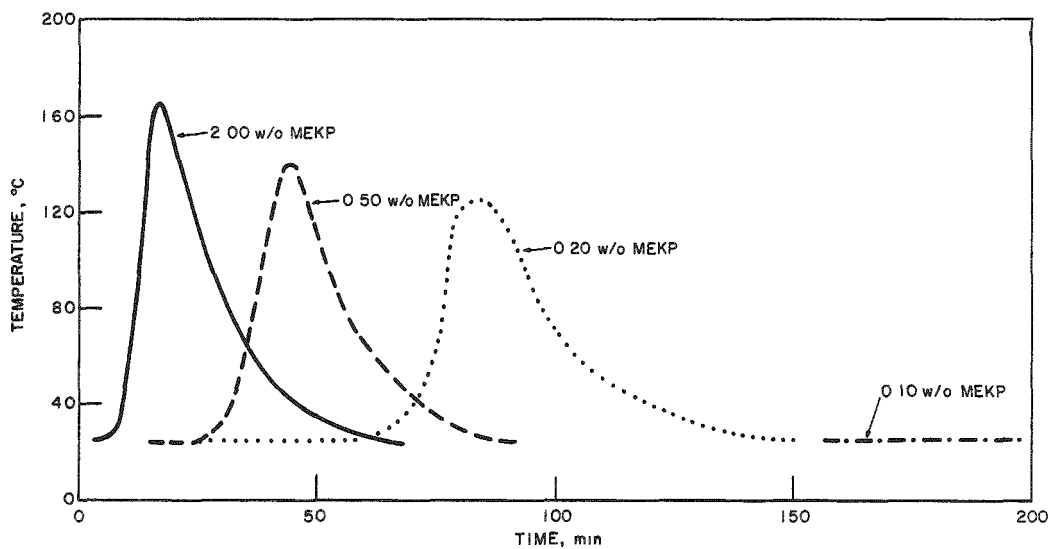


Fig. 6d. Representative Curves of Temperature versus Time after Addition of Catalyst for PE-228 in a Thin-walled Mold.

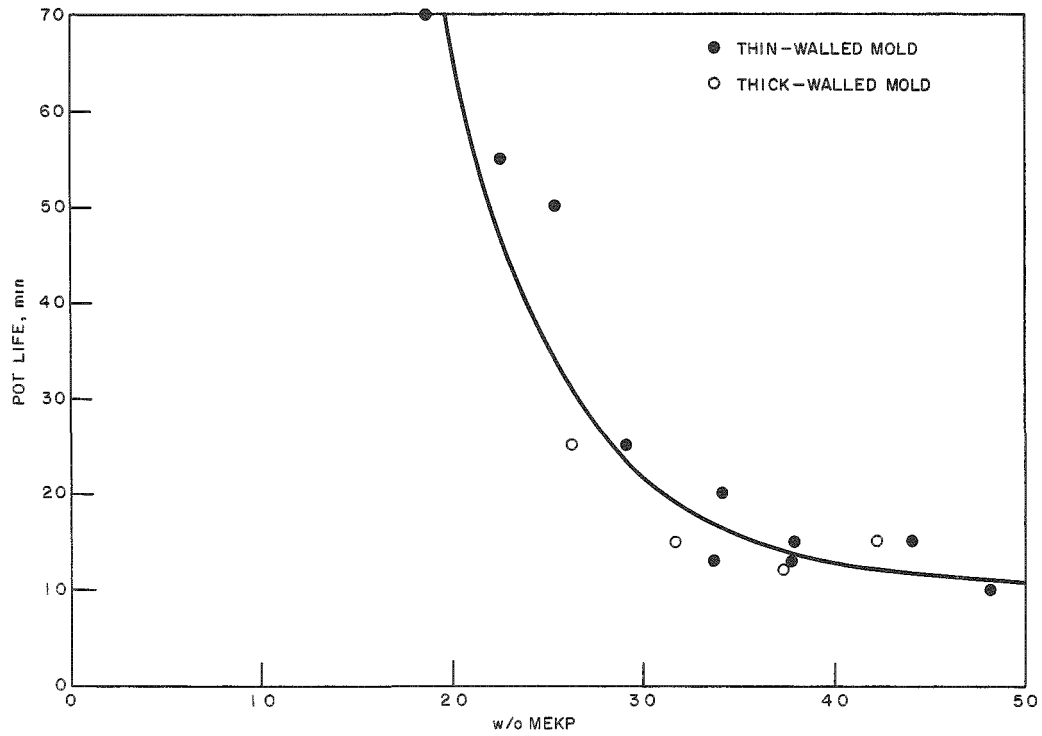


Fig. 7a. Pot Life of Polylite 8173 with Additions of MEKP

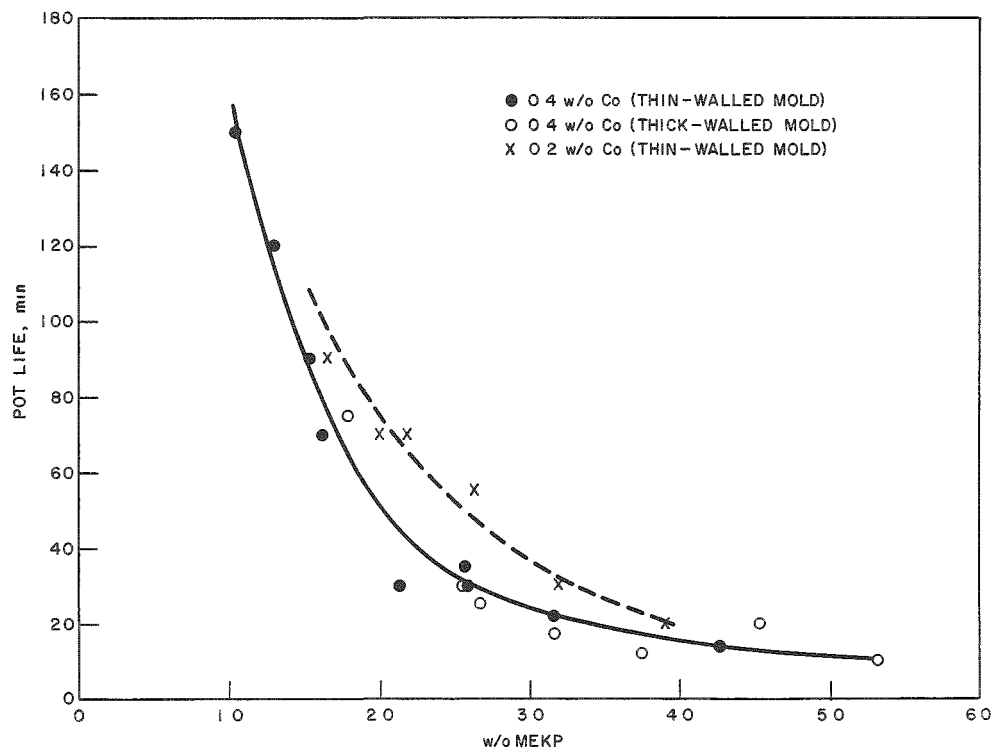


Fig. 7b. Pot Life of Polylite 8063 with Additions of MEKP

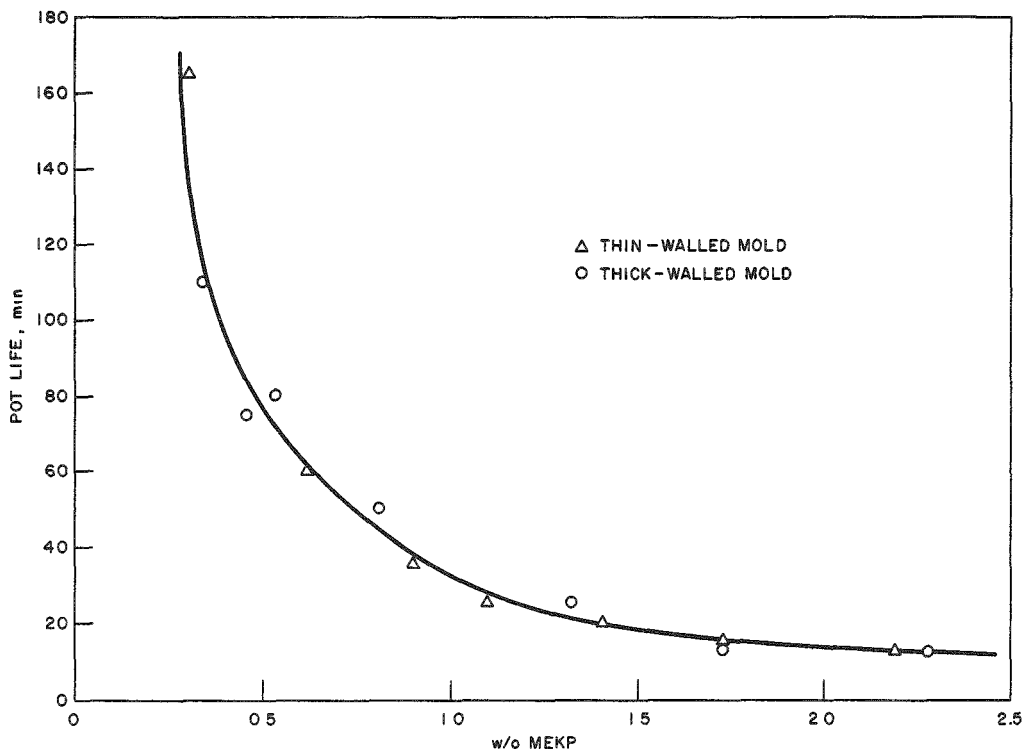


Fig. 7c. Pot Life of PE-169 with Additions of MEKP

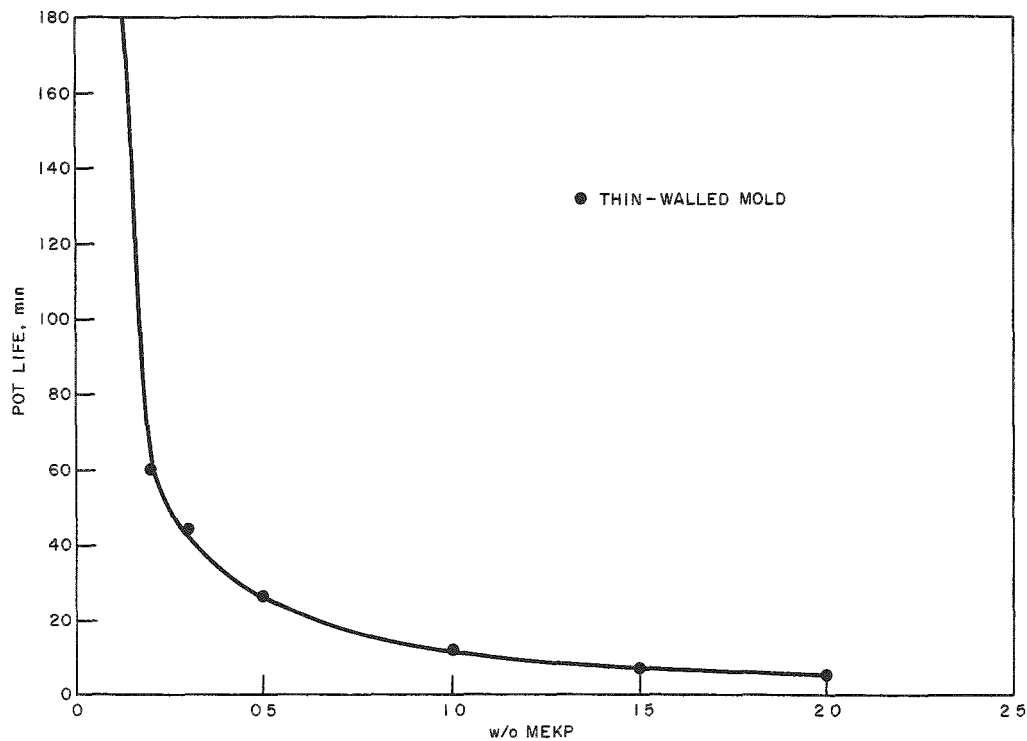


Fig. 7d. Pot Life of PE-228 with Additions of MEKP

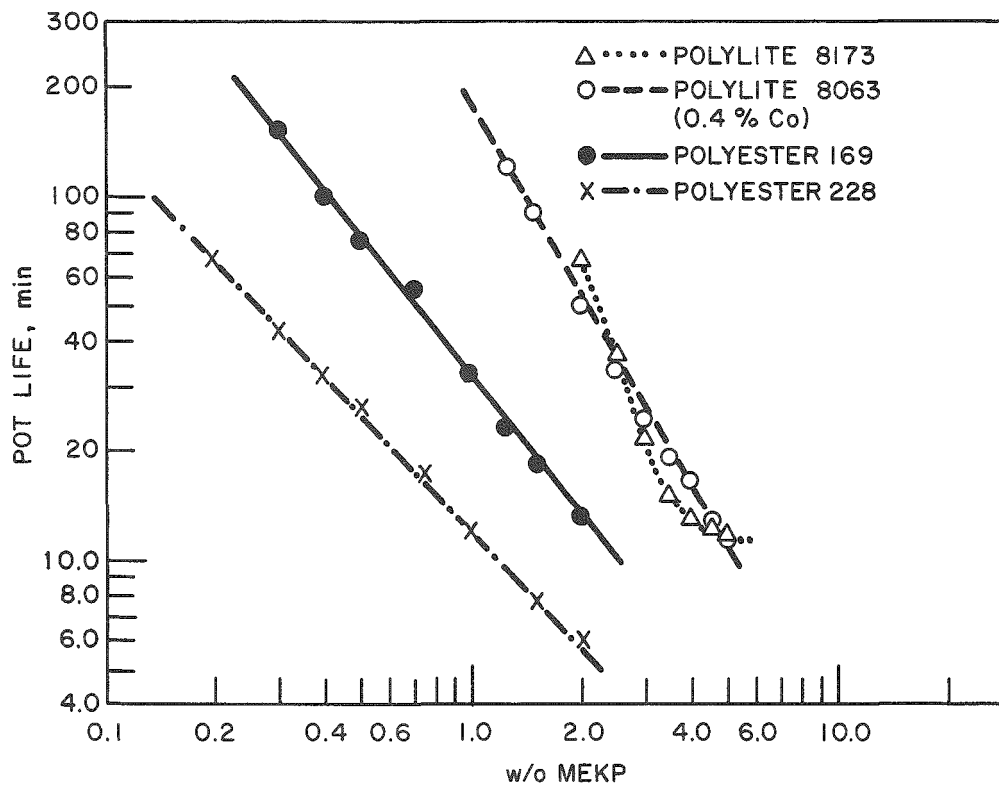


Fig. 8. Pot Life (Log Scale) As a Function of Per Cent MEKP (Log Scale)

Table IV

EQUATIONS FOR THE POT LIFE OF THE VARIOUS RESINS

Resin	Equation*
Polylite 8173**	$y = 450 x^{-2.78}$
Polylite 8063	$y = 177 x^{-1.72}$
PE-169	$y = 32 x^{-1.27}$
PE-228	$y = 12 x^{-1.07}$

*y = pot life (min); x = w/o MEKP

**Not valid for additions of MEKP above 3.5 w/o.

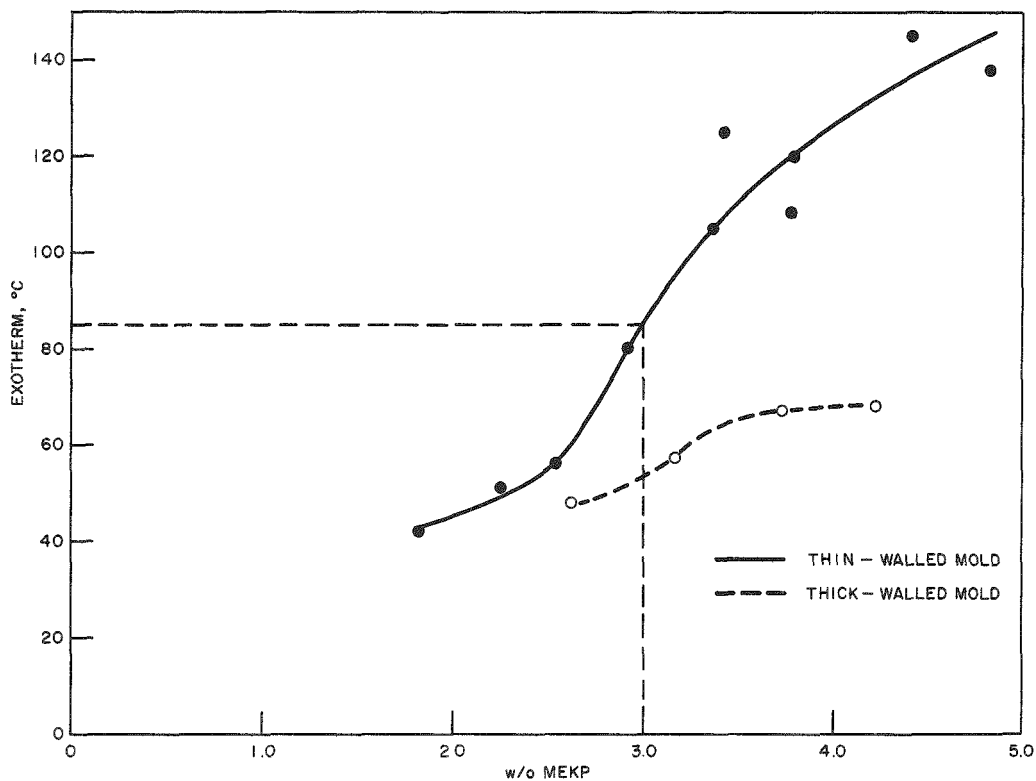


Fig. 9a. Exotherm of Polylyte 8173 with Additions of MEKP.

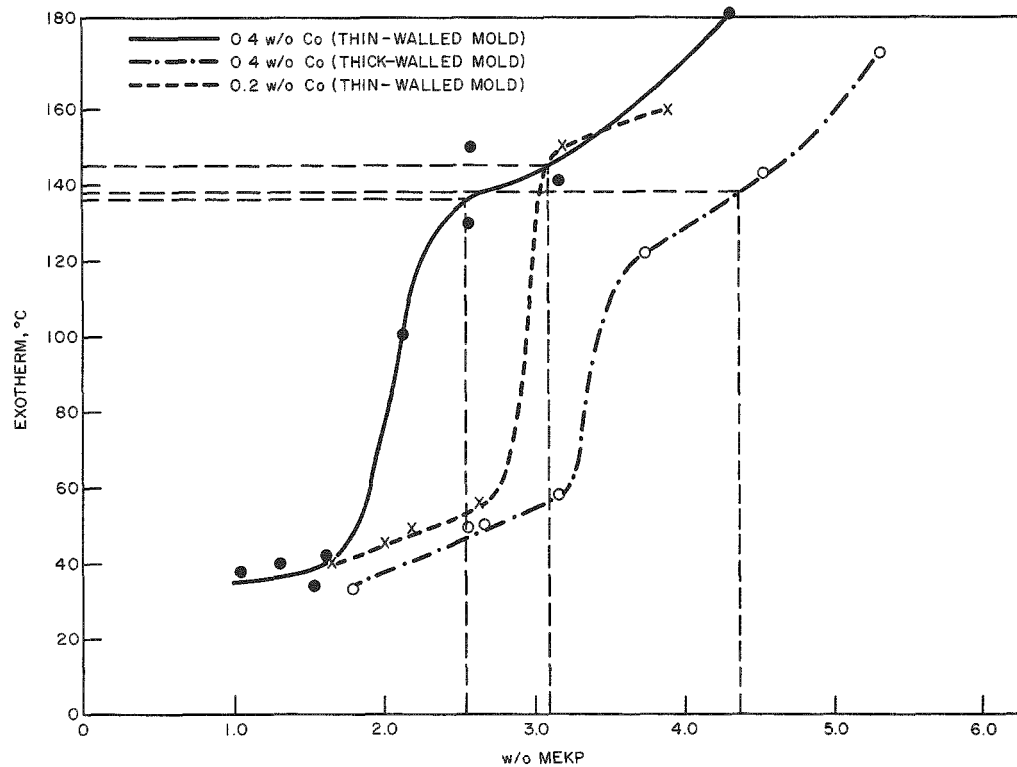


Fig. 9b. Exotherm of Polylyte 8063 with Additions of MEKP.

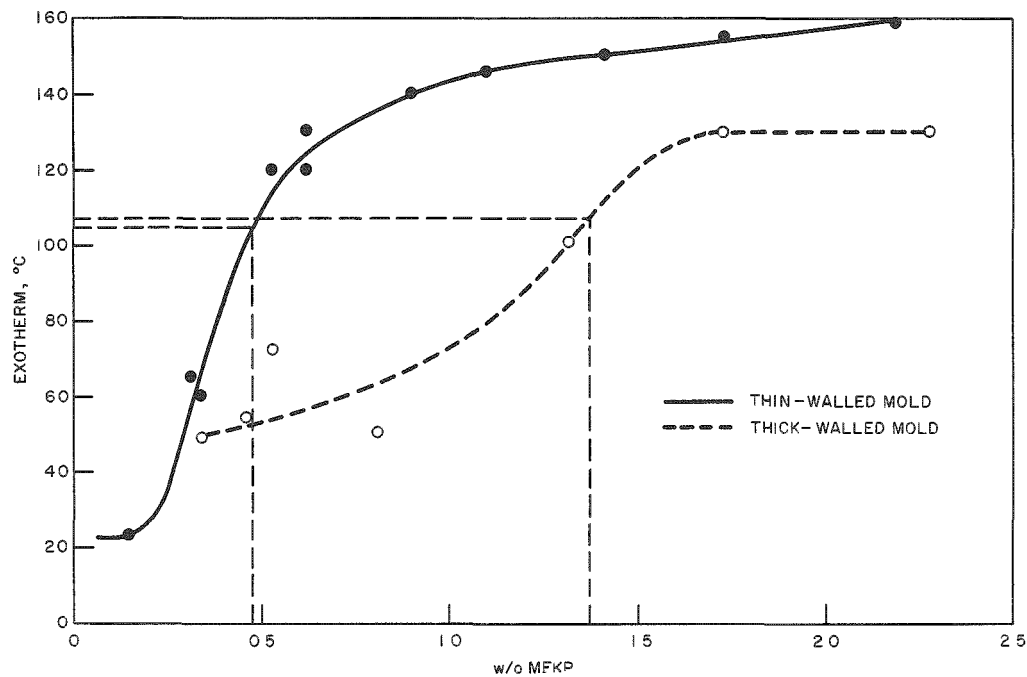


Fig. 9c. Exotherm of PE-169 with Additions of MEKP.

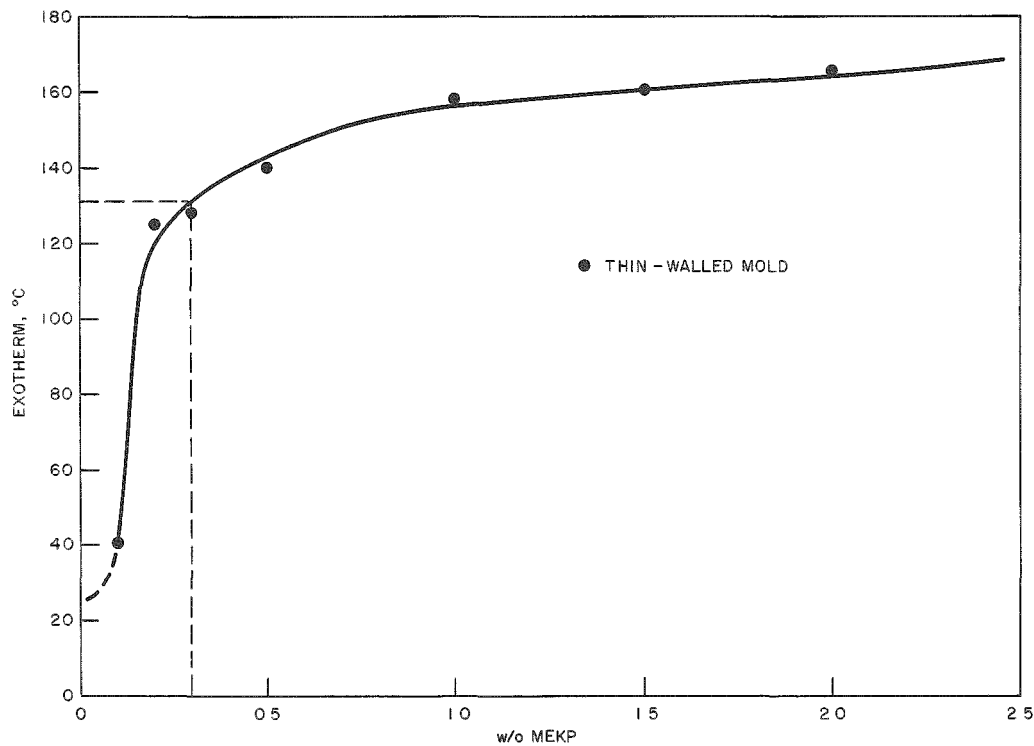


Fig. 9d. Exotherm of PE-228 with Additions of MEKP.

heat from the casting than the thin-walled mold, which resulted in a displacement of the exotherm curve for the thick-walled mold toward higher MEKP contents. This behavior was attributed to the greater thermal conductivity of Teflon ($0.0006 \text{ cal/sec-cm}^\circ\text{C}$)⁽¹⁶⁾ by a factor of ten above the conductivity of the air ($0.00006 \text{ cal/sec-cm}^\circ\text{C}$)⁽¹⁷⁾ surrounding the thin-walled Teflon molds. Casting PE-169 in a heavy steel mold with 1 w/o MEKP gave about the same value for the exotherm as found with the heavy Teflon mold. These data indicate that there is a limit to the rate of extraction of the heat generated in the casting and that this limit is reached with a heavy-walled mold of Teflon or steel. Refrigeration would probably be necessary to reduce the value of the exotherm further. Therefore, all values for the exotherm, regardless of the mold material, should probably be between the curve for the thin-walled mold and the curve for the heavy-walled mold for this casting situation. The effect of changing the mold diameter is shown in Figure 10 for Polylite 8063 and PE-169. Increasing the mold diameter from 1 to 2 in. caused an increase of 45°C in the exotherm of Polylite 8063 above the value for the 1-in.-diameter mold, whereas PE-169 had only a 10°C rise of the exotherm. Therefore, Polylite 8063 is much more sensitive than PE-169 to the quantity of resin cured.

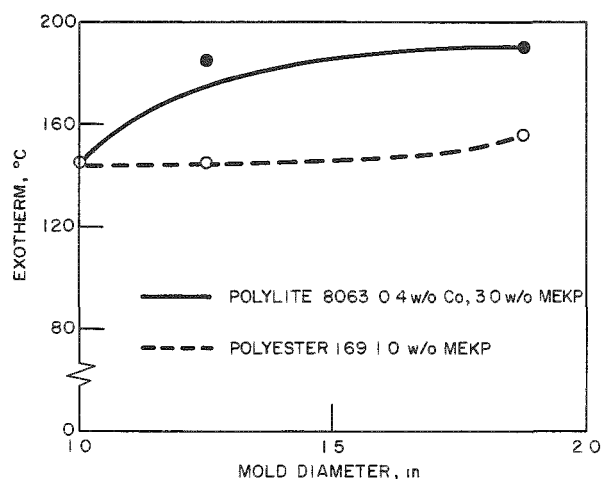


Fig. 10. Changes in the Exotherm of Polylite 8063 and PE-169 with Increasing Mold Diameters.

As shown in Figures 11a through d, the Rockwell M hardness increased with increasing additions of MEKP. The thick-walled mold of Figure 5b gave a lower value of hardness than the thin-walled mold for small additions of catalyst. The hardness values increased to the same value of hardness as found with the thin-walled mold with increased additions of catalyst for PE-169 and Polylite 8063. The low hardness values of Polylite 8173, cast in the thick-walled mold, indicate that this resin did not attain a high enough temperature for complete curing, and further additions of MEKP would be of no value as a means of increasing the properties of the resin using this curing system.

The hardness of a resin is a good measure of the extent of the cure; therefore, it can be used to evaluate the point where optimum properties have been achieved. By comparing the hardness curves of Figure 11 with the exotherm curves of Figure 9 the minimum curing temperature of each resin was estimated. In Figure 11c the maximum hardness of PE-169 is achieved with 0.47 w/o MEKP

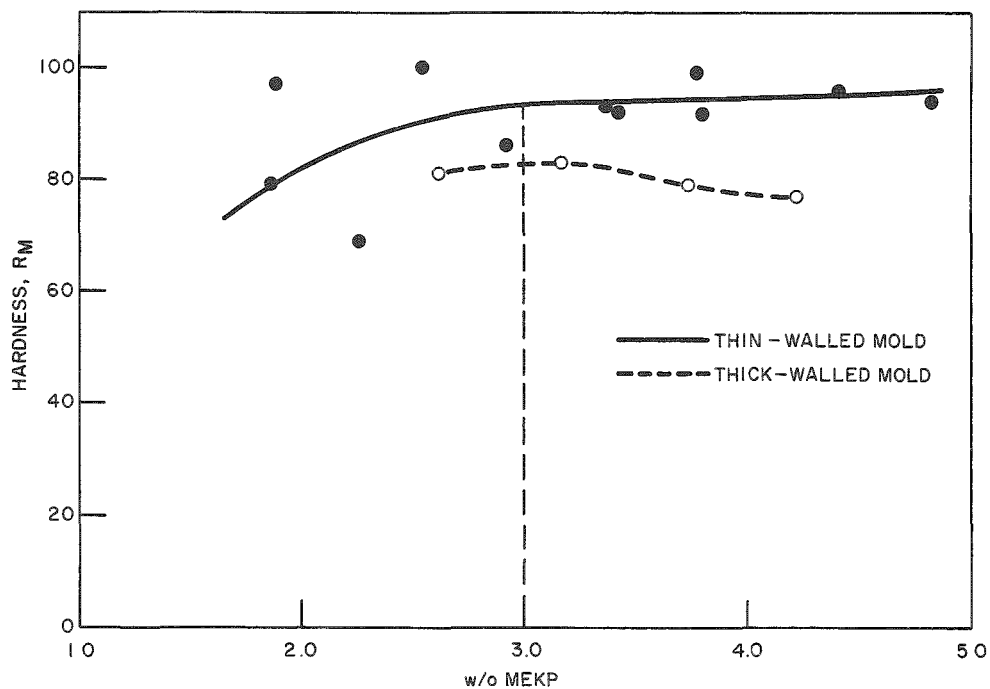


Fig. 11a. Rockwell Hardness of Polylite 8173 with Addition of MEKP.

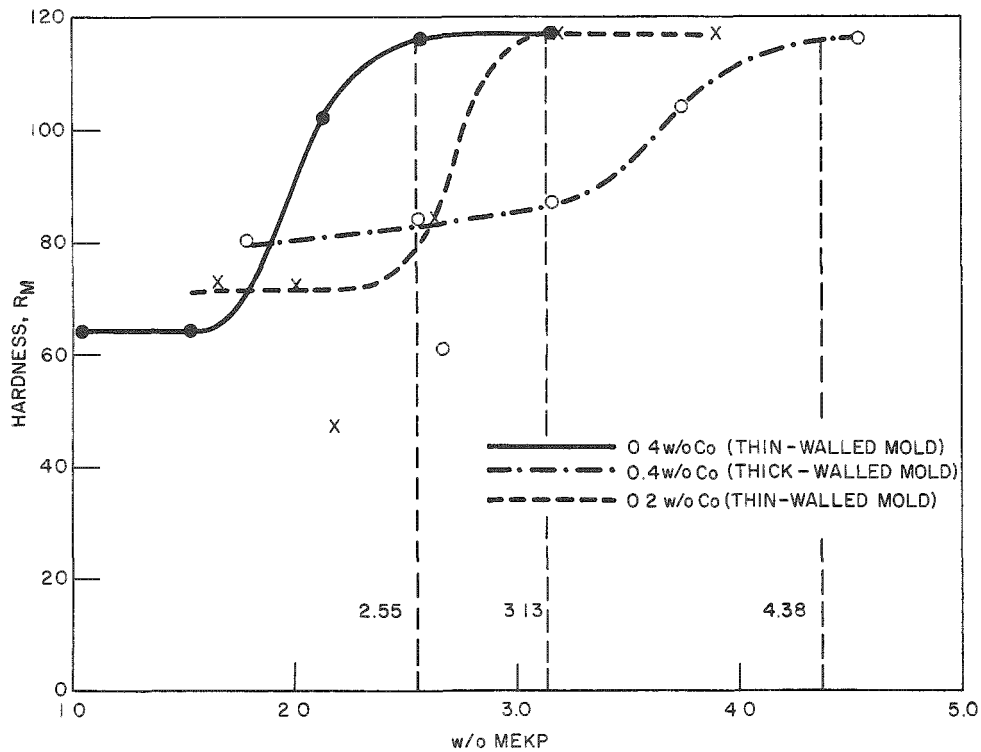


Fig. 11b. Rockwell Hardness of Polylite 8063 with Addition of MEKP.

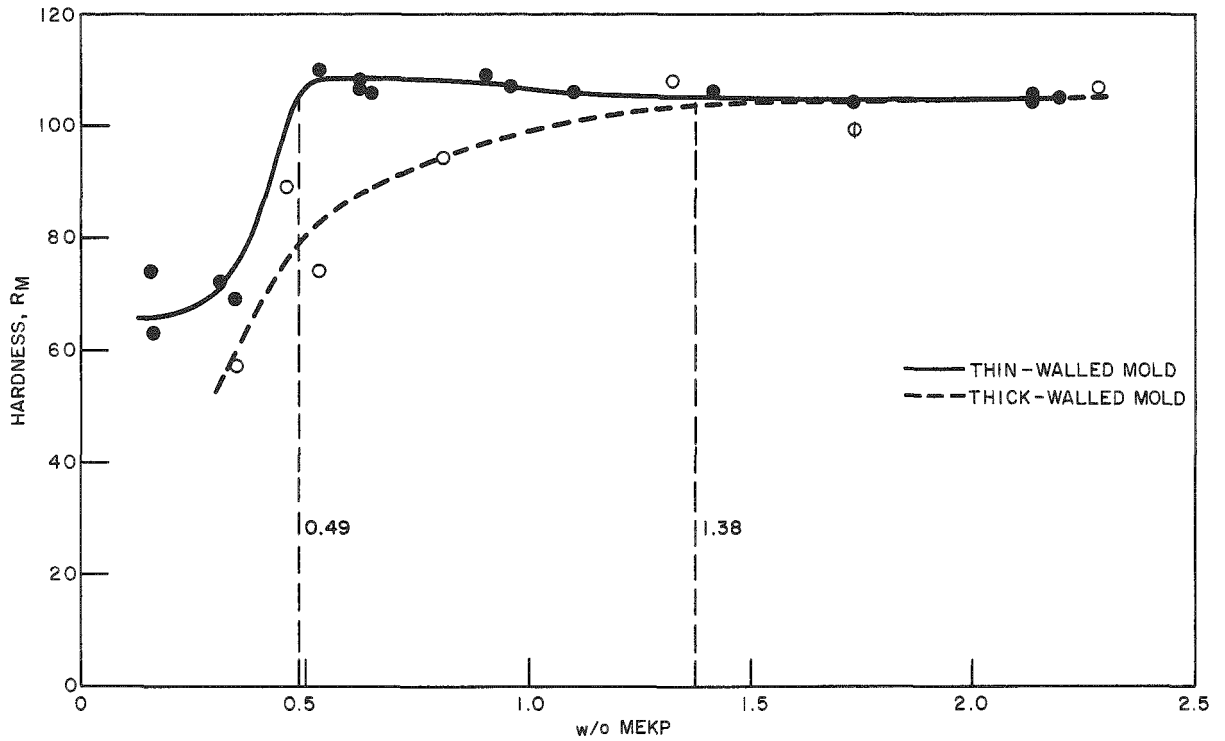


Fig. 11c. Rockwell Hardness of PE-169 with Addition of MEKP

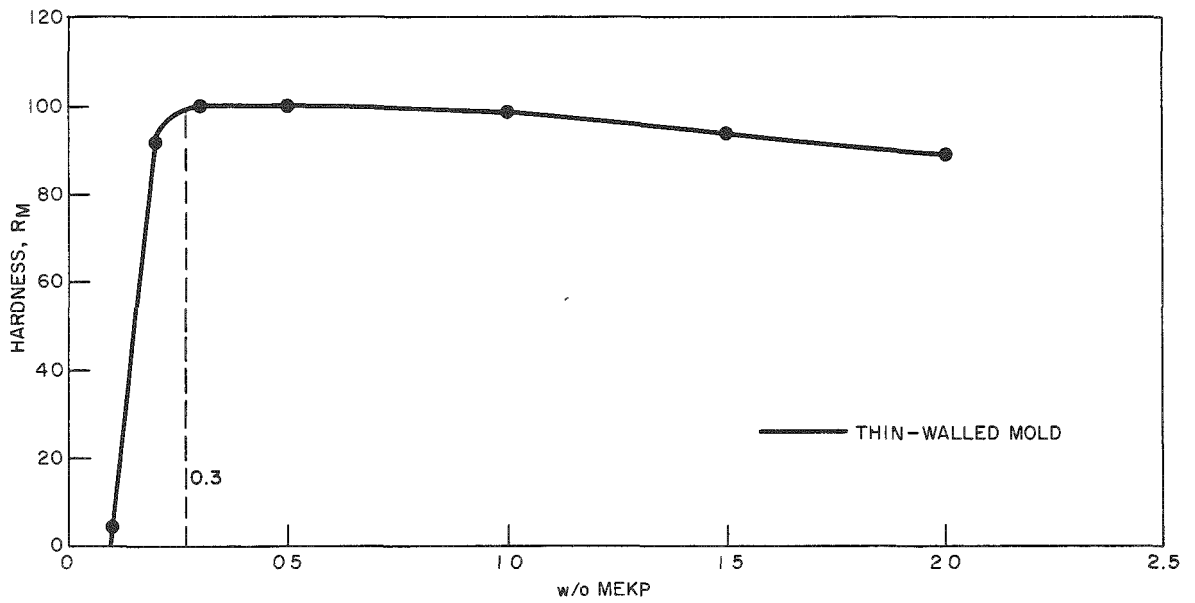


Fig. 11d. Rockwell Hardness of PE-228 with Addition of MEKP

for the thin-walled mold and 1.37 w/o MEKP for the large Teflon mold. This amount of MEKP in Figure 9c corresponds to an exotherm of 105°C for the thin-walled mold and of 107°C for the thick-walled mold. The two values are in excellent agreement. Consequently, PE-169 must reach a minimum curing temperature of about 106°C to obtain optimum properties when cured from room temperature with this catalyst system. Similarly, PE-228, Polylite 8173, and Polylite 8063 have minimum curing temperatures of 130, 85, and 140°C, respectively. The optimum points in the curves are indicated at the intersection of the dashed horizontal and vertical lines (see Figure 9a-d). Polylite 8173 cast in the thick-walled mold did not reach its minimum curing temperature with additions of MEKP up to c. 4.23 w/o; therefore, maximum hardness was not achieved.

When the additions of cobalt naphthenate solution (6% cobalt) were increased from 0.2 to 0.4 w/o for Polylite 8063, less MEKP was needed to give about the same curves as with the 0.2 w/o cobalt solution. These results are shown in Figures 7b, 9b, and 11b. Some of the scatter in the values for the curves of hardness, exotherm, and pot life can be attributed to slight variations in promotor about the required amounts of 0.2 w/o and 0.4 w/o, since these additions were only accurate to the nearest drop (approximately ± 0.03 w/o).

DISCUSSION

Bubbles

There are several properties of a resin that should be considered when bubble-free castings are desired. If the resin has a low viscosity, the bubbles will rise rapidly to the top surface of a casting long before gelling occurs. Even if the pot life is very short these resins will cure free from bubbles. PE-169, PE-228, and Polylite 8173 have low viscosities of 400, 400, and 525-650 cps, respectively. Medium-viscosity resins can be cast bubble free if the pot life is kept sufficiently long so that the bubbles have time to rise slowly. The time necessary for the bubbles to rise must be determined for each resin. Polylite 8063 has a medium viscosity (1750-2350 cps) and about 10 to 15 min in the mold is needed for the bubbles to rise. Resins that have a high viscosity and a high density usually behave like the medium-viscosity resins, and bubbles are not a problem. However, resins of high viscosity and medium density are difficult to work with, and special techniques must usually be employed to cast these resins bubble free. These techniques will not be discussed here because their elimination is one of the objects of this report.

If a metallographic specimen is placed in the mold and the resin is poured, bubbles may be entrapped around the bottom surface of the specimen. To eliminate this problem a small amount of resin should be

poured into the mold to a depth of about $\frac{1}{4}$ in. before the specimen is placed into position.

Molds

The design of the mold, the mold material, its thickness, and its environment have an appreciable effect on the exotherm of the resin, which in turn affects its properties. To predict the effect of changes in the molding conditions, each new molding situation should be analyzed with respect to the data presented above.

Polyethylene and Teflon are particularly good choices for mold materials because they both have lubricating properties which prevent the resin from adhering strongly to their surfaces. Teflon is the better of the two because it can take a higher temperature without distortion. There was no noticeable difference in the above curves when a thin-walled Teflon mold was used in place of the polyethylene mold. The thin-walled Teflon molds were difficult to make because the Teflon tended to creep away from the tool during machining. Also, the molds were easily deformed, so that castings uniform in diameter could not be made in them. Consequently, a stainless steel sleeve, $\frac{1}{16}$ in. thick, was used as a backing material for the Teflon. This design, which was found to be very satisfactory in restraining the Teflon, is shown in Figure 5c. No curves are presented for this mold; however, the curves of the exotherm and hardness for this design were found to fall slightly to the right of the curves for the thin-walled molds. The machined surface of the Teflon molds produced a translucent finish on the surface of the castings. The smooth surface of the polyethylene molds produced a smooth surface on the castings which was easy to see through.

Shrinkage

The resins discussed here shrink about 6% in volume when completely cured. If enough catalyst was added to the resin system, the outer surface of the casting heated up to a temperature which was near the center temperature and the shrinkage was uniform. However, insufficient additions of catalyst that would not give complete curing of the resin resulted in most of the curing taking place at the center of the casting, where the temperature reached its highest value. The greater shrinkage at the center of the cylindrical casting caused it to be concave about the center axis. Post-curing of these castings produced a slight change in their dimensions toward a more cylindrical condition.

Since the exotherm was measured at the center of each casting, the values reported above are the maximum for each addition of MEKP. The maximum temperature of a metallographic specimen in contact with the bottom of the mold would be expected to be lower than this value, the magnitude of the difference depending on the size. Small specimens would probably experience higher temperature rises than large specimens.

Metallographic specimens of about $\frac{1}{4}$ -in. cubes or larger usually had a layer of insufficiently cured resin surrounding them when they were cast in resin cured with additions of catalyst which would only obtain the minimum curing temperature. This insufficiently cured layer was removed by post-curing and could usually be prevented by adding a greater amount of MEKP to the resin to increase its exotherm during curing.

Corrosion Resistance

The corrosion resistance of the polyester and epoxy resins as compared with cast phenolic and acrylic resins is shown in Table V. Bakelite decomposes in strong oxidizing acids and strong alkalis like most phenolic cast resins (see Table V) whereas the epoxies and polyesters, in general, show good corrosion resistance to these solutions. The corrosion resistance of all resins, however, depends to a great extent on the degree of cure. A resin which is only partially cured, therefore, may have extremely poor corrosion resistance when exposed to certain etching solutions. To prevent the possibility of the resin being dissolved away from around the specimen, all resins used in metallographic mounts should be fully cured even though they may receive only a short-time exposure to an etching solution. It may even be necessary to post-cure specimen mounts to insure complete curing if they are to be exposed to exceptionally corrosive solutions. Of the four resins studied in this report, Polylite 8063 had the best corrosion resistance.

Table V

CORROSION RESISTANCE OF VARIOUS MOLDING RESINS*
(From *Modern Plastics Encyclopedia*, 1961)⁽⁹⁾

	Phenolic Cast Resins	Acrylic	Epoxy Cast Resin	Polyester Cast Resin
Effect of Weak Acids	None to Slight	Nil	None	None
Effect of Strong Acids	Decomposed by Oxidizing Acids	Attacked Only by High Concentration of Oxidizing Acids	Attacked by Some	None to Considerable
Effect of Weak Alkalies	Slight to Marked	Nil	None	None to Slight
Effect of Strong Alkalies	Decomposes	Attacked	Slight	Attacked
Effect of Organic Solvents	Attacked by Some	Soluble in Ketones, Esters, and Aromatic and Chlorinated Hydrocarbons	Generally Resistant	Attacked by Ketones and Chlorinated Solvents

*A.S.T.M. Test Method D543-60T(18)

Casting Techniques

Good methods of casting each resin are shown in Table VI. Method (1) is for the shortest casting times with a reasonable pot life without consideration of the exotherm. These exotherms, however, are all very close to or far below 150°C, the curing temperature of Bakelite. Method (2) is for low exotherms with reasonable total casting times. Curing of PE-228

by method (2) is not practical because the resin cannot be cured at low temperatures within a reasonable time. Table VI is by no means complete for all casting applications. It is included as a guide for those who do not want to refer to the curves. The post-curing times were not investigated extensively; therefore, these values are only approximate. A much shorter time was used for post-curing if the temperature was raised slightly, as shown by the results in Table VI. Polylite 8173 and PE-169 were cured in one hour at 60°C or in one-half hour at 70°C. Polylite 8063 was cured in 2 hr at 70°C or one hour at 80°C.

Table VI

GOOD METHODS FOR CURING POLYLITE 8173, POLYLITE 8063, POLYESTER 169, AND POLYESTER 228

Resin	w/o MEKP	w/o Cobalt	Teflon Mold	Pot Life (min)	Exotherm (°C)	Hardness (RM)	Curing Time ^a (min)	Post Cure	Total Curing Times (min)
<u>Method (1)</u>									
8173	3.75	-	Thin-walled	14	120	95	70	-	70
8173	4.25	-	Thick-walled	12	70	80	60	1/2 hr at 70°C 1 hr at 60°C	90 120
8063	2.75	0.4	Thin-walled	25	140	117	90	-	90
8063	2.75	0.4	Thick-walled	25	50	80	90	1 hr at 80°C 2 hr at 70°C	150 210
169	0.9	-	Thin-walled	35	140	108	100	-	100
169	0.9 to 2.3	-	Thin-walled	35 to 10	140 to 160	108	100 to 70	-	100 to 70
228	0.5	-	Thin-walled	26	140	100	85	-	85
228	2.0	-	Thin-walled	6	165	90	60	-	60
<u>Method (2)</u>									
8173	2.5	-	Thin-walled	45	55	90	110	1/2 hr at 70°C 1 hr at 60°C	140 170
8063	1.3	0.4	Thin-walled	110	40	64	190	1 hr at 80°C 2 hr at 70°C	250 410
169	0.3	-	Thin-walled	160	70	70	220	1/2 hr at 70°C 1 hr at 60°C	280 340

Includes time to cool back to room temperature. This time will be substantially less if the resin and mold are rapidly cooled after the peak exotherm is reached.

The most versatile resin with the best properties was PE-169. This resin has now been discontinued by the manufacturer, who replaced it with PE-228, a slightly inferior resin for this application.

Comparison with Bakelite Mounting

Mounting of metallography samples with Bakelite is a standard method which has been in use for many years. The only equipment needed is a press and the inexpensive Bakelite powder. The procedure is simple, and the finished mount is of excellent quality. However, casting of polyester resins is just as simple, and standard laboratory equipment can be used for their preparation. Reusable molds are the most expensive item, and they will vary widely in cost. If there is sufficient demand, they may be produced

and marketed at a reasonable cost by some enterprising company. The cost of the polyester resins is about the same as that of the Bakelite powder. There may be some loss of the polyester resin in storage and preparation of quantities in excess of those needed, but there is no maintenance cost of a mounting press as with Bakelite mounting.

The time for casting one specimen in Bakelite is about 10 to 15 min, depending on the warm-up time of the press. There is no decrease in the mounting time when many specimens are to be mounted and the press requires almost continuous attention. For this reason, several presses are usually operated by one technician when many specimens are to be mounted. There is a decided advantage in using the polyester resins for mounting because the only limit to the number of specimens that can be mounted at one time is the number of molds available and the pot life of the mixed resin. Bakelite mounting, however, is faster for mounting only one or two specimens, since the minimum curing times for PE-169 and PE-228 resins are about 50 min. This time may be shortened to about 30 min if the casting is fast cooled after it has reached its maximum exotherm. Many specimens can be cast in polyester resin in the time necessary for casting three specimens in Bakelite, and the technician is free to do other work while the castings cure.

Special Features

The resins selected for this study fulfill almost all the desirable properties of a metallographic mounting material. In addition, such resins also have special features which make their use even more desirable. They can be cured in a variety of ways, and their temperature rise can be controlled. The resins can be cast with a touch wire on the specimen or a touch wire can be inserted to the specimen through a hole drilled in the resin. This hole can then be refilled because the resin readily bonds to itself. The low viscosities of PE-169 and PE-228 enable them to be used for filling small holes and crevices in and around mounted specimens.

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