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PROCESS OF TREATING CAST POLYMERIC
RESIN SHEETSWillard F. Bartoe, Hulmeville, Pa., assignor to
Röhm & Haas Company, Philadelphia, Pa.No Drawing. Application April 15, 1937,
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5 Claims. (Cl. 18—48)

This invention relates to a process of treating cast vinyl and methacrylic resins to avoid the formation of the minute surface cracks that frequently appear when cast objects of these resins are placed in service. It consists in a heat treatment that removes the strains that cause these cracks.

The vinyl and methacrylic resins during polymerization undergo a substantial increase in density amounting in some instances to approximately 25%. This causes a corresponding decrease in volume. For this reason cast objects can be made from these materials only with difficulty. In the present-day methods of casting them in the form of sheets and slabs, the contraction in volume is compensated for by making the edges of the mold of a flexible or plastic material so that the two side walls can approach each other during the polymerization. Such a process is disclosed and claimed in the copending application of Otto Röhm and Walter Bauer, Serial No. 52,782 filed December 4, 1935 now Patent 2,154,639. This process while it provides a means for keeping the mold well filled during polymerization sets up surface strains in those surfaces that contact the rigid side walls. During storage or service the non-uniform release of these strains causes the formation of a myriad of minute cracks, giving the surface an undesirable "crazed" appearance.

The object of this invention is to prevent the formation of these surface cracks.

It has been found that if the sheets after they are removed from the mold are given a short heat treatment at a temperature of from 80 to 120° C., the surface does not become crazed even after extended weathering. During this heating the sheet contracts in the direction of the plane of its surfaces and undergoes a slight thickening that is equivalent thereto. It has been determined that an approximately 2% shrinkage is the maximum that the herein described process will cause and that a heat treatment that causes any shrinkage above about 1% will give the desired release in surface strains. The time of heating necessary to produce this result will vary, depending upon the temperature, the thickness of the sheet and the rate of heat transfer from heating fluid to sheet. This latter will depend upon the nature of the heating fluid; liquids, as is well known, giving more rapid heat transfer than gases. On thin sheets of poly methyl methacrylate heated to a temperature in the neighborhood of 120° C. a five or ten minute treatment will produce a non-crazing sheet, but such treatment is not recommended

because temperatures as high as this produce an undesirable softening of the sheet and make the surfaces tacky to particles of dust and dirt. A temperature of from 90° to 100° C. is preferred. In sheets of $\frac{1}{4}$ to $\frac{1}{2}$ inch in thickness a thirty minute treatment within this temperature range gives the desired result. A two hour heating at 80° C. also gives good results on sheets of this thickness. A measurement of the amount of shrinkage affords a means of determining if a particular sheet has been given a sufficient heating, a shrinkage of approximately 1% or more indicating that all strains have been removed.

It has also been found that sheets can be tested for a "crazing" tendency by subjecting them to the action of solvents or solvent vapors such as acetone, ethyl acetate, and benzene. This is conveniently done by dipping the piece to be tested in the solvent for about ten seconds and then fanning it dry. If the piece being tested contains the surface strains that cause crazing, the action of solvent accelerates the formation of the minute cracks and shows immediately whether the sheet is subject to "crazing". A test of this kind applied to a test strip cut from a larger sheet either before or after the herein described heat treatment will show whether the sheet needs to be treated and, in the case of treated sheets, whether the treatment has been sufficient to produce the desired results.

As heating fluid any gas or liquid having no chemical action on the polymeric material may be used. Liquids have the advantage of more rapid heat transfer but make necessary more cumbersome apparatus. For this reason a gaseous heating fluid is preferred except for relatively thick slabs in which the rate of heat transfer is a more important consideration. Air and kerosene are the preferred heating fluids because of their cheapness and inertness to the polymers. Water is preferable to kerosene for those polymers on which it has no effect, as for instance, the methacrylic esters. On those interpolymers that contain acrylic esters, such as ethyl acrylate, heating in water causes the formation of a whitish translucency that increases with the percentage of acrylic ester in the polymer. On such interpolymers water should not be used.

The invention is applicable to cast objects made from those vinyl and methacrylic compounds that form hard polymers, also to interpolymers of these materials and other polymerizable resin forming materials such as the acrylic derivatives. It is particularly suitable to cast objects made from the lower alkyl methacrylic esters such as

the methyl and ethyl, either when polymerized alone or in admixture with each other or with an ester of acrylic acid especially the lower methyl and ethyl esters. The term "methacrylic resin" as herein used is intended to include interpolymers in which the methacrylate is the major polymerizable component.

The invention has been described with particular reference to the treatment of cast sheets for it is in them that the undesirable "crazing" is most apparent. The principle is also applicable to objects of other shapes when such objects have been cast in molds having one or more rigid surfaces. Since the strains that cause the "crazing" are apparently the result of the force due to the polymer adhering to the mold surface acting in opposition to the force of contraction, the invention can be applied to all cast objects made under conditions in which these opposing forces exist.

To illustrate the invention and its mode of application the following table is given showing the effect of the process on sheets of polymeric methyl methacrylate of varying thickness. The sheets used were made by polymerizing methyl methacrylate in cells made of interposing spacing elements of plastic material between two sheets of glass and sealing the edges by means of paper in accordance with the disclosure of the above mentioned Röhm and Bauer application. In each instance the treatment given produced a product that showed no tendency to craze even after long exposure to the weather.

Thickness (inches)	Heating time (minutes)	Heating temperature (° C.)	Percent shrinkage
0.09	30	80	0.95
0.09	60	80	1.10
0.09	5	90	1.25
0.09	10	90	1.65
0.09	20	90	1.75
0.09	30	90	1.80
0.09	30	100	1.90
0.10	10	90	1.55
0.10	20	90	1.75
0.10	30	90	1.80
0.10	60	90	1.90
0.10	60 Plus 30	90 100	1.95
0.10	60 Plus 30 Plus 60	90 100 105	2.00
0.23	10	90	1.30
0.23	20	90	1.50
0.23	30	90	1.60
0.23	30	100	1.65
0.53	30	90	1.10
0.53	60	90	1.50
0.53	30	100	1.55

Large sheets when treated in this manner, frequently show a tendency to warp. This can be overcome by heating to a somewhat higher temperature so as to soften the sheet slightly more and allowing it to cool while resting on a soft flat surface.

It is intended that the following claims shall

include by suitable expression such modifications of the process as accomplish its purpose.

I claim:

1. In the process of forming a sheet of polymeric resin wherein a material containing a single $\text{CH}_2=\text{C}<$ group is polymerized in a mold under conditions which produce surface strains that tend to form minute cracks on the surface of the sheet, the improvement which consists in subjecting the sheet after it is removed from the mold and while it retains the shape imparted to it in the mold to a heat treatment sufficient to release the surface strains but insufficient to destroy its sheet form, said heat treatment being carried out before the appearance of the minute cracks.

2. In the process of forming a sheet of polymeric methacrylic resin wherein the methacrylic resin is polymerized in a mold under conditions which produce surface strains that tend to form minute cracks on the surface of the sheet, the improvement which consists in subjecting the sheet after it is removed from the mold and while it retains the shape imparted to it in the mold to a heat treatment sufficient to release the surface strains but insufficient to destroy its sheet form, said heat treatment being carried out before the appearance of the minute cracks.

3. In the process of forming a sheet of polymeric methacrylic resin wherein the methacrylic resin is polymerized in a mold under conditions which produce surface strains that tend to form minute cracks on the surface of the sheet, the improvement which consists in heating the sheet after it is removed from the mold and while it retains the shape imparted to it in the mold to a temperature of from 80 to 120° C. to release the surface strains, said heating being carried out before the appearance of the minute cracks and under conditions that do not destroy the sheet.

4. In the process of forming a sheet of polymeric methyl methacrylate wherein the methyl methacrylate is polymerized in a mold under conditions which produce surface strains that tend to form minute cracks on the surface of the sheet, the improvement which consists in heating the sheet after it is removed from the mold and while it retains the shape imparted to it in the mold to a temperature of from 80 to 120° C. to release the surface strains, said heating being carried out before the appearance of the minute cracks and under conditions that do not destroy the sheet.

5. In the process of forming cast objects of polymeric methacrylic resin wherein the methacrylic resin is polymerized in a mold under conditions which produce surface strains that tend to form minute cracks on the surface of the object, the improvement which consists in subjecting the cast object after it is removed from the mold and while it retains the shape imparted to it in the mold, to a heat treatment sufficient to release the surface strains but insufficient to destroy the form imparted to it by the mold, said heat treatment being carried out before the appearance of the minute cracks.

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