METHOD OF VACUUM CASTING Employing A HIGH TEMPERATURE SEALING COMPOSITION


Divided and this application Oct. 6, 1967, Ser. No. 683,054.

U.S. Cl. 164—65

5 Claims 10

Int. Cl. B22d 27/16

This application is a division of application Ser. No. 383,861, filed July 20, 1964.

This invention relates to a composition of matter containing epoxide materials. The composition serves as an excellent adhesive and is particularly useful for bonding metal to metal to produce a seal which is resistant to extensive variation in temperature.

In casting ingots of steel and alloys, gas is evolved to a greater or lesser extent during solidification of the molten metal depending upon its composition. In the production of “rimmed” steel, relatively large quantities of gas are present in a substantially uncombined state since decarburizing are not added to the metal except for minor amounts of aluminum. During solidification, the uncombined gases are continuously evolved which together with certain other factors results in a pronounced variation in properties in different sections of the ingot.

In the manufacture of “killed” and “semi-killed” steels, oxygen is caused to combine with silicon, aluminum or other decarburizing agent which is added prior to or during casting of the ingot. Though the steels treated with decarburizers have a more uniform composition and contain lesser amounts of gas in an uncombined state, enough hydrogen or other gas is present to cause the formation of minute fissures throughout the body of the ingot. Consequently, it is generally desirable to degas the various types of steel in order to obtain ingots of improved quality with respect to both physical and chemical characteristics.

In some metallurgical procedures degassing is carried out before pouring of the ingots by employing a furnace having vacuum means for removing the gaseous constituents from a batch of molten metal. In other procedures, such as vacuum casting, the gases present in a substantially uncombined state are removed from the molten metal during pouring of the ingots. An especially rapid and efficient method of vacuum casting utilizes an apparatus comprising a pouring box seated on and joined to a mold member with a sealing composition that will provide a temporary airtight seal between the box and mold during the ingot pouring interval. In this apparatus, a vacuum pump or other evacuating means is connected to a passage way in the lower part of the pouring box so that air can be evacuated from the empty mold and harmful gases can be removed from the stream of molten metal as it flows into the mold cavity. After the ingot has been poured, the seal between the box and the mold is broken and the pouring box is detached so that the ingot can be removed.

Satisfactory performance of this type of vacuum casting apparatus depends in large measure on the sealing composition used at the juncture of the pouring box and mold member. In addition to having a workable viscosity to facilitate handling and application, the composition employed must have the adhesive and cohesive properties necessary for forming an airtight seal between the metal parts. Also, it is essential that the composition have the ability to cure to a tough, elastic mass over a wide temperature range within a relatively short time. Once the composition has cured, it must be capable of withstanding temperatures between about 500° and 700° F. Without melting or deteriorating while the ingot is being poured but yet decompose upon contact with the mold up to high temperatures so that the pouring box may be readily detached after pouring has been completed.

Of the sealing compositions previously employed, the epoxide sealants have performed exceptionally well under the extremes in temperature and pressure encountered during vacuum casting. Such compositions have provided airtight seals exhibiting good resistance to flowing and deterioration during brief periods of relatively intense heat. However, it has been necessary to heat-cure prior compositions within a specific temperature range, i.e. between about 250° to 500° F., which is not always convenient in commercial production where the temperature of the molds to be assembled may vary between room temperature and 600° F.

For example, prior compositions have required prolonged curing times at room temperature and at slightly elevated temperatures so that it has been necessary to preheat molds which have cooled to these lower temperatures before applying the sealant. Otherwise, pouring schedules will be delayed since molds assembled at temperatures much below 250° F. must be allowed to stand for at least a day to insure adequate curing of the sealant. Even when the curing temperature is in the neighborhood of 250° F., some difficulty has been encountered in obtaining an effective seal due to a B-stage or incomplete cure. When the partially cured composition is exposed to high temperatures e.g., during pouring, the composition melts and the seal becomes ineffectual before degassing is complete. Above 500° F. and especially at temperatures approaching 600° F., curing of prior compositions has been accompanied by the formation of bubbles within the sealing mass and at the metal-sealant interface. While the presence of bubbles has not impaired the strength of the seal, the development of tiny air passages along the metal-sealant interface has caused a reduction in the efficiency of the vacuum. Therefore, in order to avoid bubbling, time is frequently lost during production in waiting for the molds to cool to an appropriate temperature before applying the composition.

It is, therefore, the main object of the present invention to produce epoxide sealing compositions which are capable of forming seals resistant to brief exposures to exceedingly high temperatures and yet are free from the drawbacks associated with the curing characteristics of prior compositions. This object is accomplished by providing a sealing composition comprising (I) an epoxy novolak resin, (II) a resinous polyamide, (III) an amine which is a curing agent for component (I) and, optionally, (IV) an inorganic filler. When these ingredients are combined in the proportions hereinafter described, a resinous mixture is obtained which is capable of curing to a tough but flexible mass within a relatively brief time over a wide range of temperatures extending from room temperature to about 600° F.

The compositions of the present invention find utility in a wide variety of applications for bonding many different substrates. However, they are eminently suitable for use in the type of vacuum casting apparatus which requires a temporary but highly effective airtight seal at
the juncture of the pouring box and mold member during the pouring interval. In comparison to the epoxide sealants previously employed in such an apparatus, curing proceeds quite rapidly at room temperature as well as at increased temperatures which are employed to attain a satisfactory metal-to-metal bond is obtained within a comparatively brief time at low temperatures and high temperatures alike. Since curing of these compositions proceeds to completion without a B-stage cure at room temperature as well as at elevated temperatures, there is no danger of an applied seal melting prematurely in the presence of increasing heat during pouring. Moreover, the compositions may be cured at temperatures in the neighborhood of 600° F. without bubbling to form seal free from any defects that could lead to leakage under vacuum.

In a cured state, the compositions are hard and tough but sufficiently flexible and compressible to withstand cracking from mechanical or thermal shock. They are further characterized by high internal bond strength and the ability to form unusually strong bonds with metal or other substrates. At temperatures between about 500° and 700° F., they resist melting and thermal degradation for the time period which corresponds to an ingot pouring interval and thereafter decompose to the extent necessary for permitting removal of the pouring box from the mold member.

The attached drawings illustrate a vacuum casting apparatus in which the sealing compositions of the present invention find particular utility.

FIGURE 1 is a vertical cross-sectional view of an assembled vacuum casting apparatus with the composition of the present invention forming a seal at the juncture of a removable pouring box and ingot mold.

FIGURE 2 is an enlarged fragmentary cross-sectional view of the seal.

Referring more particularly to the drawings, an ingot mold is denoted at 1 which has a cylindrical cavity 2 tapering at its lower end and an annular groove 3 in its upper surface. The groove 3 extends around the circumference of the upper surface of the mold and provides a support for the removable pouring box generally designated at 5. Within the groove 3 is a sealant 4 which is the sealing composition of the present invention. The sealant 4 forms a vacuum-tight seal between the mold 1 and the pouring box 5.

The pouring box 5 is divided by a transverse wall 6c into an upper section comprising a basket 5a for receiving the molten metal to be poured and a lower section comprising a vacuum chamber 5b communicating directly with the mold cavity 2. The transverse wall 6c contains a pouring aperture 6 which is closed by a fusible closure member 7. When molten metal is deposited in the basket 5a, the closure 7 becomes fused and will allow the molten metal to pass through the aperture 6 and through the vacuum chamber 5b into the mold cavity 2.

An annular refractory hot top 8 is positioned within the vacuum chamber 5b and is attached to the mold. A tube 9, which is connected to a vacuum pump (not shown), is tightly secured within an opening (not shown) located in the side wall which leads into the vacuum chamber 5b.

In assembling and operating the apparatus described above, the epoxide sealing composition of the present invention is deposited in the annular groove contained in the upper surface of the mold body. Thereafter, the pouring box with the aperture in the transverse wall tightly closed by a fusible closure member is seated on the mold so that the lower edge of the vacuum chamber is positioned and embedded in the mass of sealing composition contained within the groove. The assembly is then allowed to stand for a time sufficient to allow complete curing of the composition. The specific time period required for the composition of the present invention depends upon the temperature of the mold being assembled. For the quantity of sealant ordinarily, curing may be accomplished in about two to seven hours at room temperature and in ten minutes or less at a temperature of about 200° F. with somewhat faster curing being obtained with further increases in temperature. After curing is complete and with the aperture tightly closed, the vacuum pump is started so that air is evacuated and a vacuum created in the mold and vacuum chamber. The molten metal to be poured is deposited in the basket which comprises the upper section of the pouring box using a transporting ladle or other conventional means. In the presence of the hot metal, the closure member becomes fused and allows the metal to flow through the aperture in the transverse wall and through the vacuum chamber into the mold cavity. Because of the high vacuum exerted in an area close to the stream of metal being introduced, the stream is disrupted into a spray of fine particles from which harmful gases may be readily removed. The effectiveness in removing substantially all the uncombined gases is further aided by the continual ebullition of metal collecting in the mold which results from the high vacuum exerted close to the mold cavity.

If desired, degassing may be continued after pouring is complete since the pouring interval is relatively brief and about twenty minutes or so lapses before heat of maximum intensity has been conducted into the mold and into the area of the seal. This may be accomplished by maintaining or renewing the vacuum after a suitable closure is inserted in the basket and positioned over the upper side of the aperture in the transverse wall. After the degassing operation has been terminated and after the heat in the area of the seal is sufficient to decompose the sealing composition, the pouring box is disengaged so that the solidified ingot may be removed from the mold cavity.

The effectiveness of the seal formed by the present composition is demonstrated by the degree of vacuum obtained. Ordinarily, an absolute pressure of twenty microns is reached in less than five minutes and micron gauge readings below ten microns and, frequently as low as four microns, are reached in ten minutes. Readings below ten microns are consistently obtained when the pumping means shuts off which clearly illustrates the ability of the compositions to form an essentially vacuum-tight seal.

The resins useful as component (I) in preparing the compositions of the present invention have the following theoretical molecular structure:

They are produced by the epoxidation of a novolak base resin which is a resole type or permanently fusible resin formed by the condensation of a phenol and an aldehyde, e.g. phenol and formaldehyde, under acid conditions. While any of the epoxy novolak resins are suitable for use in preparing the high temperature sealants, it is preferred to use a fluidized resin of this type in order to facilitate mixing with the other components particularly, with fillers are employed and to allow greater ease of application. A particularly suitable epoxy novolak resin is the Dow's experimental resin QX 2638.1 which has an epoxide equivalent weight of about 172-175, a molecular weight of 2.2 times the epoxide equivalent weight and a viscosity between about 8,000 and 10,000 centipoises at approximately 30° C. The epoxide equivalent weight is the weight of resin in grams which contains 1 gram chemical equivalent of epoxy and is determined by reacting a
known quantity of resin with a known quantity of hydrochloric acid and back-titrating the remaining acid to determine its consumption.

As component (II), any of the lower molecular weight resins may be used which have an amine number greater than 85. The "amine number" may be defined as the milligrams of potassium hydroxide equivalent to the amine alkalinity in one gram of sample. Polyamide resins having an amine number much below 85 are not sufficiently reactive with the epoxylated novolak resin to impart the cured properties desired in the present system.

The resins polyamide employed are prepared by methods well-known in the art by condensing polymeric polypeptide fat acids, such as dimerized linoleic acid, and polyamides and, in general, have a viscosity between about 40 and 575 poises at 40° C. as measured on a Brookfield Viscometer Model RVP at 20 r.p.m. using a #3 spindle. Typical of the resins which may be used are the liquid polyamide resins, "Versamid 115," "Versamid 125," "Versamid 140" and the like. Semi-fluid resins, such as "Versamid 100," may also be employed but are preferably used in admixture with the liquid resins in minor proportions so that the resulting resin mix will have a workable room temperature viscosity. The preparation of the "Versamids" is described in U.S. Patent No. 2,379,413.

In the present system the polyamides are used primarily for their plasticizing or flexibilizing effect on the cured composition. In order to obtain cured compositions having the strength and flexibility necessary for resisting mechanical shock, the resinous polyamide is used in amounts varying between about 50 and 100 parts by weight on the basis of 100 parts by weight of epoxy novolak resin. When less than 50 parts is used, the cured composition tends to become glassy while compositions containing more than 100 parts of the polyamide resin become brittle, easily cracked materials.

Though the polyamide resin imparts cured properties to the composition, the use of an amine curing agent for the epoxy novolak resin is essential for obtaining a relatively rapid cure over a wide temperature range. The amines and mixtures of amines employed as component (III) have the following structure:

\[ R-N-(CH_2)_m-(NH(CH_2)_n)_p-NR_2 \]

where \( m \) and \( n \) each are integers having a value of 1 to 6, \( R \) is hydrogen or a lower alkyl group having 1 to 4 carbon atoms, such as methyl, ethyl, propyl or isopropyl groups, and \( p \) is at least two active hydrogens. Illustrative amines include ethylene diamine, diethylene triamine, triethylenetetramine, tetraethylenepentamine, hexamethylenetetramine, 3-diethylaminopropylamine and the like.

The amount of amine used should be sufficient for completely curing the epoxy novolak resin. Normally, the amount employed is in slight excess of the stoichiometric amount needed for cure since some of the amine is frequently lost through volatilization during curing. On the other hand, large excesses should be avoided since excess amine tends to interfere with crosslinking.

In addition to the above essential ingredients, it is advantageous to incorporate fillers into the composition to adjust the viscosity and to increase thermal conductivity thereby lowering the coefficient of thermal expansion and promoting a more even cure. Among the fillers which can be used are aluminum oxide, mica, asbestos, atomized aluminum, iron and copper. Fibrous materials such as finely divided asbestos tend to counteract differences in thermal expansion between the composition and the bonded metal. Amounts of the fillers up to about 15% by weight based on the total composition have been found satisfactory for the present composition. Amounts above 15% by weight tend to impair the cohesive properties and internal bond strength of the cured system.

The following examples are given to illustrate the present invention. All quantities given are in parts by weight unless specified otherwise.

**Example 1**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component A—</td>
<td></td>
</tr>
<tr>
<td>Liquid polyamide resin ¹</td>
<td>(amine No. 230–246; viscosity—575 poises at 40° C.)</td>
</tr>
<tr>
<td>Liquid polyamide resin ²</td>
<td>(amine No. 330–360; viscosity—100 poises at 40° C.)</td>
</tr>
<tr>
<td>Diethylene triamine</td>
<td></td>
</tr>
<tr>
<td>Component B—</td>
<td></td>
</tr>
<tr>
<td>Epoxylated phenol-formaldehyde resin ³ (epoxide equiv. wt. 172–175; molecular wt. approx. 375–385; viscosity—8,000 to 10,000 c.p.s. at 30° C.)</td>
<td>50</td>
</tr>
<tr>
<td>Asbestine—finely divided magnesium silicate (filler)</td>
<td>12.5</td>
</tr>
</tbody>
</table>

¹ "Versamid #115." ² "Versamid #125." ³ Dow experimental resin Q 2635.1.

Component A was prepared by mixing the polyamide resins and amine in a paddle mixer until a homogeneous mixture was obtained. In order to facilitate mixing, the ingredients may be slightly heated.

Component B was prepared in the same manner by adding the asbestine to the epoxy novolak resin with stirring and continuing stirring after addition was complete until the asbestine was homogeneously dispersed throughout the resin.

Component A and Component B were then thoroughly mixed together and the resulting composition was poured into the groove of a cast iron ingot mold having a temperature of approximately 600° F. The pouring box was then seated on the mold so that the lower edge of the box was embedded in the sealing composition contained within the groove. After curing, which was achieved within a few minutes, the mold and lower section of the box were evacuated and molten steel was introduced into the mold cavity. The ingot pouring interval was approximately five minutes and the vacuum attained was in the neighborhood of about four microns absolute pressure.

It was found that the seal formed by this composition decomposed after 45 minutes which allowed ample time for the second degassing after pouring was completed. At the same time, decomposition occurred within a reasonable interval so that the pouring box and mold could be reassembled for a new run at the production rates desired in commercial operations.

In order to study the over-all curing characteristics of the above composition, portions of this composition were deposited in aluminum cups and allowed to cure at various temperatures. The time required for complete curing at the temperatures selected was as follows:

<table>
<thead>
<tr>
<th>Room temperature (72° F.)</th>
<th>hrs.</th>
<th>150° F.</th>
<th>hrs.</th>
<th>200° F.</th>
<th>hrs.</th>
<th>225° F.</th>
<th>hrs.</th>
<th>300° F.</th>
<th>hrs.</th>
<th>400° F.</th>
<th>hrs.</th>
<th>450° F.</th>
<th>hrs.</th>
<th>500° F.</th>
<th>hrs.</th>
<th>600° F.</th>
<th>hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td></td>
<td>8</td>
<td></td>
<td>8</td>
<td></td>
<td>5</td>
<td></td>
<td>4.4</td>
<td></td>
<td>3.4</td>
<td></td>
<td>2.4</td>
<td></td>
<td>1.2</td>
<td></td>
<td>1-2</td>
<td></td>
</tr>
</tbody>
</table>

After curing, the compositions were inspected for voids and other imperfections, and it was found that none of the cured samples showed any evidence of bubbling including the sample cured at 600° F.

The heat resistance of the above composition when cured at various temperatures was also studied by curing strips of the composition at a given temperature and then placing the cured strips in a furnace maintained at a selected temperature until the strips showed signs of melting prior to decomposition. The curing temperatures em-
ployed and the time elapsing before the strips began to flow at a selected elevated temperature are set forth in Table I below.

<table>
<thead>
<tr>
<th>Curing temperature</th>
<th>Time interval before flowing</th>
<th>Min. at 60°F.</th>
<th>Min. at 700°F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temp. (72°F.)</td>
<td>74</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>200°F.</td>
<td>30</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>400°F.</td>
<td>19</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>500°F.</td>
<td>14</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

When strips of composition cured at room temperature, 200°F., 400°F., and 500°F. were placed in a furnace maintained at 600°F., all withstood melting and decomposition for a period of about 43 to 50 minutes.

From the results obtained above, it is readily apparent that the composition of Example 1 may be cured rapidly over a broad temperature range. Between 150°F. and 600°F., curing may be accomplished in 15 minutes or less and at room temperature (approximately 72°F.) a complete cure was obtained in 7 hours in contrast to curing times of a day or more required by prior sealants. Moreover, the composition may be cured at temperatures ranging between about 500°F. and 600°F. without the formation of bubbles within the sealing mass or at the metal-sealant interface.

It is also apparent that the composition when cured at either low or high temperatures resisted flowing and decomposition for at least 3 minutes when subjected to relatively intense heat. The ability of the composition to withstand temperatures between about 630°F. and 700°F. for periods up to 15 minutes assures sufficient time for degassing of the metal after the pouring operation, though heat of this intensity rarely reaches the sealing area of the mold in less than fifteen minutes after pouring is completed.

**Example 2**

**Ingredients:**

- **Component A**
  - Liquid polyamide resin 1
  - Triethylene tetramine
  - Parts by weight
  - 24
  - 7.1

- **Component B**
  - Epoxidized phenol-formaldehyde resin 2
  - Asbestos (filler)
  - Parts by weight
  - 50
  - 10

1 "Versamid #115."
2 Dow experimental resin QA 2635.1.

Component A and Component B of Example 2 were prepared and then thoroughly mixed together in the same manner as described in Example 1 above.

Portions of the composition of Example 2 were placed in aluminum cups and some samples cured at room temperature and others at 200°F. and 500°F., respectively. The time required for complete curing of each sample at these temperatures was 107 minutes at room temperature, 7 minutes at 200°F., and 254 minutes at 500°F.

The heat resistance of each of the cured samples was measured in the same manner described in Example 1. The cured strips of composition were removed from the aluminum cups and placed in a furnace maintained at a selected elevated temperature until the strips showed signs of flowing. The results obtained are set forth in the following table.

<table>
<thead>
<tr>
<th>Curing temperature</th>
<th>Time interval before flowing, minutes at—</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°F.</td>
<td>15</td>
</tr>
<tr>
<td>700°F.</td>
<td>7</td>
</tr>
<tr>
<td>Room temp. (72°F.)</td>
<td>7</td>
</tr>
<tr>
<td>200°F.</td>
<td>5</td>
</tr>
<tr>
<td>500°F.</td>
<td>6</td>
</tr>
</tbody>
</table>

From the foregoing examples and tables, it can be seen that the compositions of the present invention are especially useful for forming metal-to-metal seals exhibiting excellent heat resistance. The compositions, while having the pot life necessary for commercial operations, which obviates heating of the cooled casting molds as previously required in vacuum casting techniques. At temperatures in the range of 500°F. to 600°F., the compositions will cure within a few minutes to form seals free from voids or other imperfections caused by bubbling. After curing, the compositions resist melting and decomposition for at least three minutes at temperatures in the range of 600°F. to 700°F. whether cured at low or high temperatures. Since heat of this intensity does not reach the seal area of the mold for about fifteen to twenty minutes after pouring, an additional period of several minutes at temperatures between about 600°F. and 700°F. is assured for continuing the degassing, if desired. At the same time, the cured composition will decompose after a reasonable interval at relatively high temperatures so that the seal can be broken and the molding apparatus promptly reassembled for another pouring operation.

**We claim:**

1. In a method of vacuum casting which comprises
   - (A) providing a metallic casting mold having an annular groove in its upper surface,
   - (B) depositing a flowable curable sealing composition in said groove, said composition being comprised of an epoxy novolak resin, a liquid resinous polyamid and an amine which is a curing agent for said novolak resin,
   - (C) embedding the lower edge of a vacuum chamber in the sealing composition residing in the groove of said mold, said chamber having an upper closable aperture,
   - (D) allowing the sealing composition to cure to form an airtight seal at the juncture of the vacuum chamber and mold,
   - (E) closing the aperture in said vacuum chamber and evacuating the air therefrom to create a vacuum,
   - (F) introducing molten metal through the aperture
in said chamber and into said casting mold while maintaining the seal at the juncture of said mold and chamber for at least a time until all the metal is introduced, and

(G) subjecting said seal to heat of increasing intensity being conducted from the molten metal through said mold into the area of said seal to thermally destroy the same.

2. A method according to claim 1 wherein the sealing composition is composed of

(1) an epoxy novolak resin having an epoxide equivalent weight between about 172 and 175 and a molecular weight between about 378 and 385,
(2) 50 to 100 parts by weight of a liquid resinous polyamide per 100 parts of novolak resin having an amine number of at least 85 per 100 parts by weight of novolak resin, and
(3) an amine which is a curing agent for said novolak resin in an amount in slight excess of that necessary to react stoichiometrically with said resin, said amine having the structure

$$R_2N-(CH_2)_m-(NH(CH_2)_n)_p-NR_2$$

where m and n each are integers having a value of 1 to 6, p has a value of 0 to 6, R is selected from the group consisting of hydrogen and lower alkyl groups having 1 to 4 carbon atoms, said amine having least two active hydrogens.

3. A method according to claim 2, wherein the composition includes an inorganic filler in an amount up to about 15% by weight based on the total weight of the composition.

4. A method according to claim 3, wherein the filler in the composition is finely divided magnesium silicate and the amine is a member selected from the group consisting of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, hexamethylene tetramine, 3-diethylamino-1-propyl amine, and mixtures thereof.

5. A method according to claim 4 wherein the sealing composition is composed of

(1) 100 parts by weight of an epoxy novolak resin having an epoxide equivalent weight between about 172 and 175, and a molecular weight between about 378 and 385,
(2) 92 parts by weight of a liquid resinous polyamide having an amine number between about 230 and 246 and a viscosity of about 575 poises at 40° C.,
(3) 4 parts by weight of a liquid resinous polyamide having an amine number between about 330 and 360 and a viscosity of about 100 poises at 40° C.,
(4) 10.8 parts by weight of diethylene triamine, and
(5) 2.5 parts by weight of finely divided magnesium silicate.

References Cited

UNITED STATES PATENTS

1,679,582  8/1928 Nelson 164—65
2,934,452  4/1960 Sternberg 260—18
2,999,825  9/1961 Peerman et al. 260—18
3,170,887  2/1965 Ramos 260—18
3,305,901  2/1967 Gero 164—65

WILLIAM J. STEPHENSON, Primary Examiner.
E. MAR, Assistant Examiner.

U.S. Cl. X.R.

164—137
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,430,679
March 4, 1969

John J. O'Brien et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 15, after "polyamide," cancel "per 100 parts of novolak resin".

Signed and sealed this 31st day of March 1970.

(SEAL)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents