

- [54] **METHOD OF PREPARING THERMOSET POLYMER COATED-WAX IMPREGNATED CELLULOSIC STOCK**
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- [58] Field of Search **117/65.2, 92, 143 R, 155 R, 117/155 UA, 157, 158, 168, 155 L**

[56] **References Cited**
UNITED STATES PATENTS

2,791,569	5/1957	Backlund	117/155 X
3,353,992	11/1967	Grenley et al.	117/138.8
3,428,591	2/1969	Lewis	117/158 X
3,515,691	6/1970	Arabian	117/158 X
3,554,950	1/1971	Sauer	117/158 X
3,558,542	1/1971	McDonald	260/27
3,577,373	5/1971	Kremer et al.	260/23
3,580,736	5/1971	Moyer et al.	117/158 X

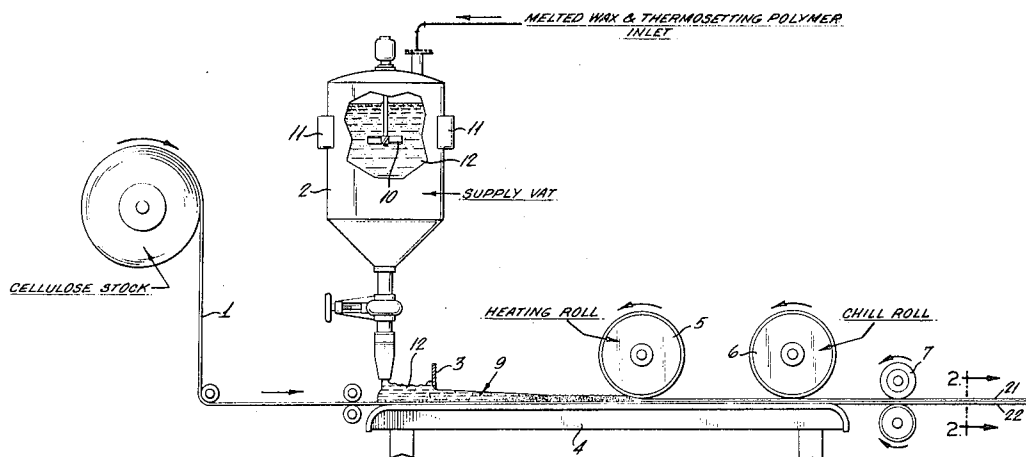
3,791,856 2/1974 Duling et al. 117/155 UA

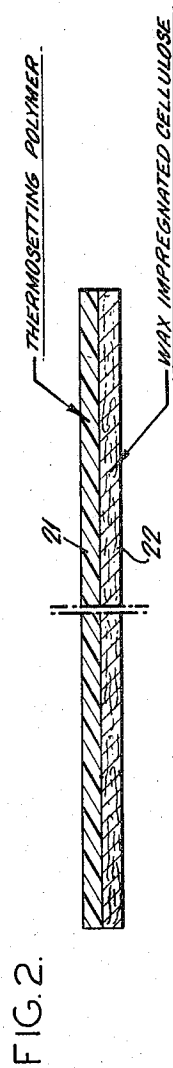
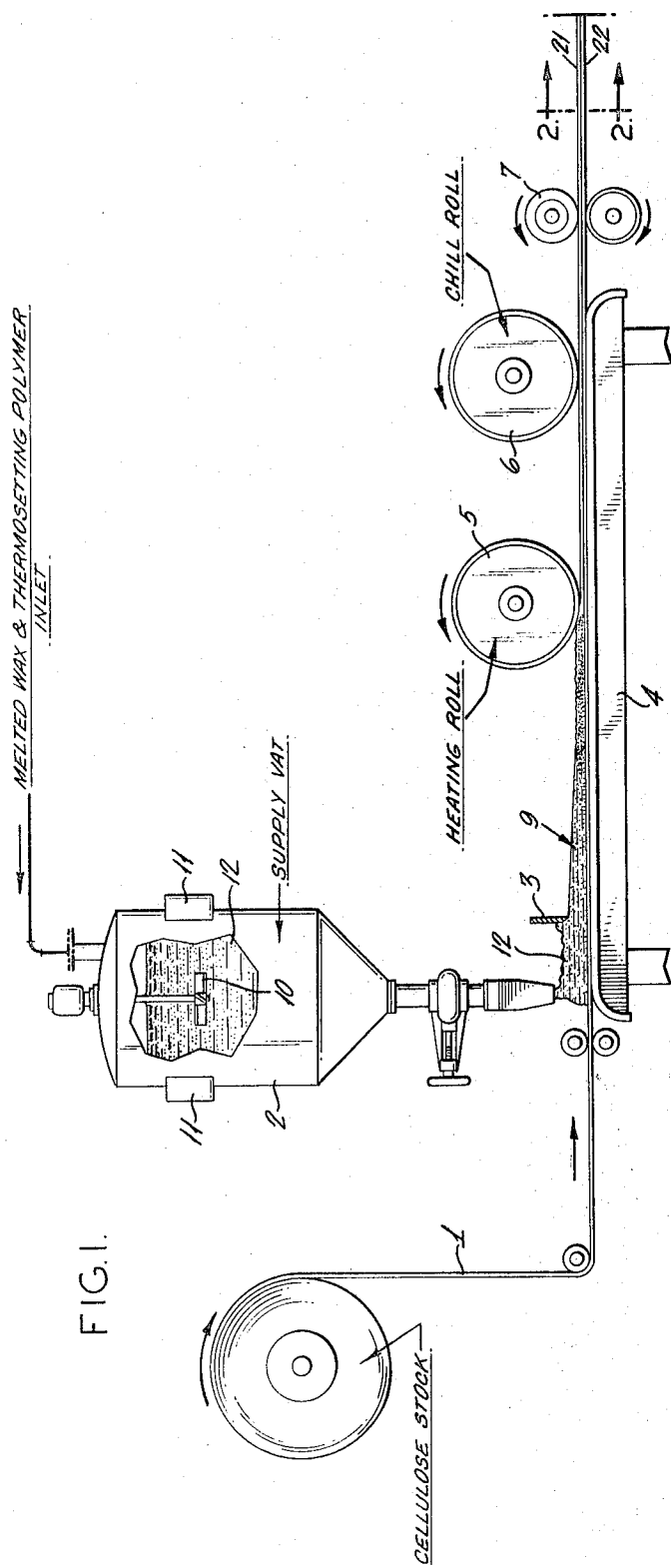
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[57] **ABSTRACT**

Porous cellulosic stock can be coated with a thermoset polymer while being impregnated with a wax by this invention. A dispersion of solid particles of the precursor of a thermoset polymer in molten wax is applied to cellulosic stock at a temperature below the conversion temperature of the precursor. This treated cellulosic stock is then heated to a temperature above the conversion temperature of the precursor and subjected to pressure. The resulting laminated product is polymer coated-wax impregnated cellulosic stock. The solid precursor used must be substantially insoluble in the molten wax at a temperature below the conversion temperature of the precursor and must be convertible below a temperature which would degrade the stock. This product has utility as a packaging material comprising a high water vapor barrier coupled with a tough, scuff-resistant, non-blocking surface.

10 Claims, 2 Drawing Figures





METHOD OF PREPARING THERMOSET POLYMER COATED-WAX IMPREGNATED CELLULOSIC STOCK

BACKGROUND OF THE INVENTION

The present invention provides a method for impregnating porous cellulosic stock with wax, which imparts a high water vapor barrier to the stock, while coating the stock with a thermoset polymer which imparts a tough, scuff-resistant, non-blocking surface to the stock. The method can be used to apply a thermoset polymer coating to one or both surfaces of the stock.

United States patent application Ser. No. 163,041, by Duling et al. filed July 15, 1971, now U.S. Pat. No. 3,791,856, patented Feb. 12, 1974, discloses a method of preparing a thermoplastic coated-wax impregnated cellulosic stock. Specifically, the aforementioned method comprises applying a dispersion of thermoplastic polymer particles in molten wax to cellulosic stock at a temperature below the melting point of the polymer. The treated cellulosic stock is then heated to a temperature above the melting point of the thermoplastic polymer and subjected to pressure. The thermoplastic polymer used must be substantially insoluble in the molten wax at a temperature below the melting point of the polymer and must be fusible below a temperature which would degrade the stock. As used herein, a thermoplastic polymer refers to material that softens, even flows, when raised to an elevated temperature but returns to a solid state when cooled to room temperature.

Surprisingly, it has been found that a porous cellulosic stock can be coated with a thermoset polymer while being impregnated with a wax by this invention. As used herein, a thermoset polymer refers to a solid material that solidifies or sets irreversibly when heated. The solid material is also referred to as a precursor of a thermoset polymer. This irreversible property is usually associated with a cross-linking reaction of the molecular constituents induced by heat. Also, this irreversible reaction can also be caused by condensation induced by heat.

SUMMARY OF THE INVENTION

Porous cellulosic stock can be impregnated with wax and coated with a thermoset polymer by the method described herein. The solid particles of the precursors of a thermoset polymer must be substantially insoluble in the molten wax at a temperature below the conversion temperature of the precursor. A dispersion of the thermoset polymer in molten wax, at a temperature below the conversion temperature of the precursors, is applied to the porous cellulosic stock. Afterwards, the temperature of the applied coating is raised to above the conversion temperature of the precursor but below the degradation temperature of the stock, and pressure is applied causing the precursor particles to convert into a continuous thermoset polymer coating. The resulting wax impregnated cellulosic stock coated on one or both surfaces with a thermoset polymer has utility as a packaging material with a high water vapor barrier. In addition, the coated surfaces are resistant to scuffing, are non-blocking and have a glossy attractive finish. The coating of solid thermoset polymers can be one of the following classes: allylic, epoxide, phenolic, amino, polyamide, thermoset polyurethane and cross-

linkable polyvinylchloride. These thermoset polymers are described in MODERN PLASTICS ENCYCLOPEDIA Vol. 47, 1970 - 1971.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically illustrates one method of applying the wax dispersion to cellulosic stock in accordance with the invention.

FIG. 2 is a cross-sectional view of the finished laminated product.

DESCRIPTION

A method of preparing a thermoset polymer coated-wax impregnated cellulosic stock according to this invention is illustrated in FIG. 1. Finely divided thermoset precursor and solid wax are placed in a suitable container 2 (supply vat). These thermoset precursors can also be referred to as thermosetting polymer. The temperature of the solid precursor and wax in the supply vat is raised to above the melting point of the wax but below the conversion temperature of the precursor by a suitable heater 11. After the wax melts, sufficient agitation is applied by a conventional mixer 10 to keep the finely divided solid uniformly distributed throughout the molten wax. The dispersion in the container 2 (supply vat) is transferred, in this illustration, by gravity to the cellulosic stock 1 in front of the doctor blade 3. As soon as the dispersion contacts the stock, absorption of the wax in dispersion by the stock begins. The cellulosic stock 1 moves on a smooth flat surface 4 towards the doctor blade 3. The temperature of the molten wax dispersion is maintained below the conversion temperature of the precursor particles. The doctor blade 3 causes a predetermined thickness of dispersion 12 to be deposited on the stock 1. The covered stock, as indicated by 9, travels to a hot roll 5. The pressure of the hot roll 5 spreads the heated particles into one continuous coating and the heat converts the precursor into the thermoset polymer. Afterwards, the stock is cooled by cold roll 6 and rollers 7 move the finished product 8 away.

FIG. 2 is a cross-sectional view along section AA in FIG. 1 of the finished product 8 prepared by the above-described method. The substrate layer 22 represents the cellulosic stock 1 now impregnated with wax from the wax dispersion 12. The substrate layer 22 is covered with a continuous thermoset polymer coating 21 (also referred to a thermosetting polymer), the polymer being from the wax-precursor dispersion 12. Because substantially all of the wax is absorbed by the stock 22 and the precursor is substantially insoluble in the molten wax, the continuous coating is substantially only thermoset polymer.

Since the conversion step in the coating operation occurs after quantitative separation of the wax from the polymer, the barrier properties of these coatings are those of the thermoset polymer film combined with those of the wax-impregnated cellulosic stock.

In practicing this invention, the cellulosic stock must be able to absorb wax at a reasonable rate. Thus a cellulosic stock coated with a substance or impregnated with a substance which would substantially slow down the wax impregnation rate would be unsatisfactory. Typical wax absorption times for coated and uncoated stocks are shown in the following Table I.

Table 1

Wax Absorption Time of Various Cellulosic Stocks			
Stock ⁽²⁾	Thickness, mils	Surface Coating	Wax Absorption ⁽¹⁾ Time, Minutes
Kraft liner board	8.5	No	1
Corrugated board	10	do.	1
Cup board	14	do.	3.5
Chip board	33	do.	0.5
Oil can cardboard	26	do.	0.5
Freezer carton			
Regular density	10	do.	3
Medium density	18	do.	0.5
Paper plate	20	do.	1.5
do.	20	do.	3 to 4
Oil can cardboard	26	Yes	6 to 10
do.	28	Yes and printed	50 to 70
Freezer carton			
Regular density	10	Yes	35
Medium density	18	do.	20 to 22.5
Bread wrapper	2.5	—	12
Glassine paper	1.33	—	100

⁽¹⁾Time required for a 0.1 ml. drop of wax to be absorbed into a test sheet at 160°F.

⁽²⁾These stocks are defined in the DICTIONARY OF PAPER, 3rd Edition, American Paper and pulp Association, 1965.

The date in Table 1 indicates that a coated stock such as coated oil can cardboard, having a wax absorption time of 6 to 10 minutes, would be a stock which probably should not be used with this invention. However, a coated stock such as medium density freezer carton, having a wax absorption time of 20 to 22.5 minutes, would be a stock which normally would not be used with this invention.

The pulp used to make the various cellulosic stocks that can be used in this invention can be derived from a suitable source such as wood, reclaimed paper, cotton fibers and other fibers such as manila hemp, jute, etc.

Cellulosic stock also refers to wood and porous products made therefrom. Examples of such products are hardboard, particleboard, insulating board and plywood. These boards are defined in *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, Kirk-Othmer, 2nd Edition, Vol. 21, Section Wallboard.

The wax used herein can be a petroleum wax obtained by any one of the processes described in Chapter 5 of *THE CHEMISTRY AND TECHNOLOGY OF WAXES* by A. H. Warth, 2nd edition and can be any one of the refined or unrefined petroleum waxes described in the same chapter. Synthetic waxes that can be used are described in Chapter 6 of the aforementioned reference.

Petroleum wax is commercially available with a wide range of physical properties. Paraffin waxes are available with melting points from about 126°F. to 153°F. (ASTM D87), oil contents from about 0.1 to about 1.2 percent (ASTM D721), penetration at 77°F. from about 9 to 40 (ASTM D1321), specific gravity at 212°F. from about 0.756 to 0.767 (ASTM D287). Microcrystalline waxes are available with melting points from about 151°F. to 193°F. (ASTM D127), oil contents from about 0.4 to about 1.5 percent (ASTM D721), and specific gravity at 212°F. from about 0.786 to 0.795 (ASTM D287). While these different petroleum waxes will be absorbed at different rates by various cellulosic stocks, this invention can be used with any petroleum wax fraction that will be absorbed by the stock.

If the solid particles of the precursors of a thermoset polymer which are soluble in molten wax at a temperature below the conversion temperature of the precursor is used with this invention, the following problem arises. On coating the stock some of the combination of wax and precursor could be absorbed by the stock. Furthermore, any of the combination remaining on the surface of the stock could form a relatively soft polymer wax coating on the surface of the stock. Thus to avoid the heretoforementioned problems the precursors which are used with this invention must be substantially insoluble in the molten wax at a temperature below the conversion temperature of the precursor. In addition the precursor must resist conversion at the temperature required to maintain the dispersion in the fluid state.

Examples of thermoset precursors which are substantially insoluble in molten wax at a temperature below the conversion temperature of the precursors are as follows: diallyl phthalate, diallyl isophthalate, diallyl maleate, diallyl chlorendate, each of which are examples of allylics; typical polyepoxides are those based on the reaction of epichlorohydrin with bisphenol-A, or the reaction of epichlorohydrin with the phenolic groups of a phenol-based novolac resin; thermoset polyurethanes are of ASTM type III but without the usual solvent system; and polyamic acid precursor which upon heating form a polyamide, both the precursor and polyamide are defined in *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY* 2nd Edition, Kirk-Othmer, Supplement Volume; and crosslinkable polyvinylchloride. These solid precursors of thermoset polymers are defined as to chemical composition, physical properties, and methods of preparation in *MODERN PLASTIC ENCYCLOPEDIA*, Vol. 47, 1970/1971.

The thermoset precursor used in this invention, when added to the wax, is in the form of finely divided solid particles. If the particles are too large, say passing through 3 mesh but remaining on 20 mesh, the resulting dispersion is unstable in that the particles settle out rapidly causing problems during the application of the dispersion to the stock. All references to mesh herein refer to U.S. Sieve Series. Even if this settling problem can be overcome, the resulting polymer coating on the stock is of non-uniform thickness and is not continuous; that is, there are some areas where there is no polymer coating. Thus, while this invention is operable if all the precursor particles pass through a 20 mesh, it is preferable that all particles pass through 100 mesh and even more preferable that all particles pass through 200 mesh. Particle size distribution also influences dispersion stability and dispersion viscosity. At the same wax-polymer ratios a wide range particle distribution, compared to a narrow range particle distribution, tends to have a great viscosity and hence greater stability. The limits as to particle size distribution range can be easily determined by those skilled in the art.

The viscosity of the dispersion depends on the concentration of the precursors in the wax, the affinity of the precursor for wax and particle size and shape. Spherical particles, as formed in suspension polymerization, flow more readily than those irregularly shaped, such as those resulting from grinding.

The weight ratio of the solid precursor to the wax used in this invention depends on dispersion stability and dispersion viscosity which in turn depends on polymer particle size and particle size distribution. Satisfac-

tory weight ratios are 5 to 65 parts by weight of finely divided precursor and 35 to 95 parts by weight of wax, the preferable weight ratios are 10 to 55 parts by weight of finely divided precursor and 45 to 90 parts by weight of wax.

The preliminary step in practicing this invention is to prepare the dispersion. The solid wax is placed in a suitable container and heated until the wax becomes molten; but the resulting temperature should not exceed the conversion temperature of the precursor being used. After the wax melts, the solid precursor of a thermoset polymer is added; mild agitation is usually necessary to form the dispersion. Alternatively, both the solid wax and the solid particles can be placed in a container and heated together to a temperature below the precursor's conversion temperature. Immediately after the dispersion has been prepared, it can be used or it can be cooled and the resulting solid used at a later time. The permissible temperature range used to prepare the dispersion depends on the melting point of the specific wax being used and the conversion temperature of the specific precursor being used.

The dispersion consisting of molten wax and precursor particles is applied to the surface of a cellulosic stock as defined herein. The application of a uniformly thick layer of dispersion to the stock can be obtained by using a doctor blade, or by extruding (curtain coating), or by a roll coater or some other suitable equipment.

As soon as the dispersion touches the stock, the wax starts to be absorbed by the stock. The length of time during which this absorption occurs before the application of additional heat and pressure depends on the equipment used, the wax absorption rate of the stock and the amount of wax applied per surface area of stock. This length of time can range from almost zero to many minutes. An example where this length of time is many minutes long is illustrated by the following. After the dispersion containing a relatively large percentage of wax is applied, the additional heat and pressure is not applied until substantially all the wax is absorbed by the stock. During this long intervening period, the temperature of the dispersion must be above the melting point of the wax but below the conversion temperature of the precursor. A minor amount of wax can remain unabsorbed so that the precursor particles remain evenly distributed on the stock during movement of the stock.

After the application of the dispersion to the stock, the coated stock is subjected to additional heat to raise the temperature of the material on the surface to above the conversion temperature of the precursor and subjected to pressure to cause the precursor particles to form the desired continuous smooth coating. As soon as a uniform smooth coating is assured, sufficient heat is applied. However, the maximum temperature of the material cannot exceed a temperature which causes degradation of the stock. For paper, discoloration and/or loss of strength would be examples of degradation caused by too high a temperature. Thus for paper stocks the maximum temperature would be about 500°-550°F. This degradation temperature limitation means that certain thermoset polymers could not be used with the method defined herein because the precursors conversion temperature exceeds the degradation temperature of the stock undergoing coating.

The application of this heat to raise the temperature of the dispersion can precede the application of pressure by some finite time or can be simultaneous with the pressure. The amount of pressure applied depends on the type of thermoset precursor and ability of the stock to withstand the applied pressure without undesirable deformation. During this step any wax remaining on the surface is absorbed by the stock.

Subsequently the stock can be allowed to cool or can be cooled by suitable heat removal device. A cold roller would be one example.

The heretoforementioned description discusses only the application of the precursor of resulting thermoset polymer coating surface. In a similar manner a thermoset polymer coating could be formed on the other side of the cellulosic stock. In this embodiment the amount of wax applied in the first treatment should not be such that the stock becomes completely impregnated with wax. In other words, during the application of the coating on the second side, the partially wax-impregnated stock has to absorb at least most of the wax contained in this other wax-precursor dispersion. The resulting product in this case is a wax-impregnated cellulosic stock having both surfaces coated with the same thermoset polymer or with different thermoset polymers.

The following example illustrates this invention.

EXAMPLE

Sixty-six parts of petroleum wax were placed in a suitable container, and the temperature of the wax was raised to 150°F. which was above its melting point but below the fusion point of the solid thermoset polymer to be added. To the molten wax was added 34 parts of diallyl phthalate powder a precursor of an allylic thermoset polymer. The resulting dispersion of molten wax and solid diallyl phthalate particles maintained at 150°F., was spread on paperboard (18 mil, 218 lbs/3,000 ft.² ream) by use of a Gardner knife set to a spacing of 15 mils between the paper and the knife. The raw-coated paperboard was pressed between platens heated to 350°F with aluminum foil in contact with the raw-coated face of the paperboard. A pressure of about 200 psig was maintained for about 5-10 seconds. The treated paperboard was removed from the press, cooled and stripped of the aluminum foil.

Upon examination, the treated paperboard was found to substantially absorb all the wax; the polymer surface was continuous and hard. The polymer surface did not soften by subsequent heating to 350°F indicating cross-linking, one type of conversion.

The petroleum wax used in these examples had the following inspections:

Melting point, ASTM D87	126°F.
Oil content, ASTM D721	0.4
Color, Saybolt, ASTM D156	+29
Penetration at 77°F., ASTM D1321	18
Viscosity, SUS at 210°F., ASTM D446	38.8
Specific gravity at 212°F., ASTM D287	0.760

Similar results can be obtained with other (1) uncoated stock, (2) petroleum waxes, (3) precursors of thermoset polymers of the following type: allylic, epoxides, thermoset polyurethanes (ASTM III) without solvent, polyamide, and crosslinkable polyvinylchloride.

The invention claimed is:

1. Method of preparing an article comprising a wax-impregnated porous cellulosic stock having a thermoset polymer coating, which comprises:

- a. establishing a heterogeneous composite of solid particles of the thermosetting polymer in finely divided form and molten wax, said particles having the following properties:
 1. a conversion temperature between the melting point of the wax and the degradation temperature of the substrate;
 2. substantial insolubility in the molten wax at a temperature below the conversion temperature of the polymer;
 - b. applying a coating of said heterogeneous composite to a porous cellulosic substrate at a temperature above the melting point of the wax but below the conversion temperature of the thermosetting polymer; the amount of coating being regulated so that at least most of the wax therein is adsorbable in cellulosic substrate;
 - c. heating said particles to a temperature between the conversion temperature of the thermosetting polymer and the degradation temperature of the substrate and applying pressure thereto to form a continuous thermoset polymer layer on the surface of the porous substrate;
 - d. and thereafter cooling the resultant article.
2. Method according to claim 1 wherein said heterogeneous composite contains 5 to 65 parts by weight of finely divided thermosetting polymer and 35 to 95 parts by weight of said wax.

3. Method according to claim 1 wherein all the finely divided thermosetting polymer is finer than 100 mesh.

4. Method according to claim 1 wherein all the finely divided thermosetting polymer is finer than 200 mesh.

5. Method according to claim 1 wherein the wax is a petroleum wax.

6. Method according to claim 5 wherein heterogeneous composite contains 5 to 65 parts by weight of finely divided thermosetting polymer, said polymer being finer than 100 mesh.

7. Method according to claim 1 wherein said solid thermosetting polymer particles are allylic, polyepoxide, phenolic, amino, polyamide, thermoset polyurethane of ASTM type III, or cross-linkable polyvinylchloride.

8. Method according to claim 7 wherein the heterogeneous composite contains 5 to 65 parts by weight of finely divided thermosetting polymer, said polymer being finer than 100 mesh, and the wax is petroleum wax.

9. Method according to claim 8 wherein the solid thermosetting polymer is formed from diallyl phthalate, diallyl isophthalate, diallyl maleate or diallyl chloronate.

10. Method according to claim 9 wherein said heterogeneous composite contains 10 to 55 parts by weight of finely divided polymer and 35 to 90 parts by weight of wax.

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