United States Patent Office

2,878,503

Patented Mar. 24, 1959

2,878,503

BRUSH

Jerome L. Been and Martin M. Grover, Rutherford, N.J., assignors to Rubber and Asbestos Corporation, Bloomfield, N.J., a corporation of New Jersey

No Drawing. Application July 3, 1953
Serial No. 366,052

4 Claims. (Cl. 15—193)

This invention relates to brushes and to bristle setting compounds used in the manufacture of brushes, and particularly those compounds intended for use with synthetic bristles.

A typical brush comprises four principal components. One of these comprises the clusters of fibers known as bristles. The second component is the clamping shell known commonly as the ferrule. The third element of a brush consists of the means for holding the bristles together and within the ferrule, and the fourth component is the brush handle.

Until recently brush bristles consisted chiefly of animal fibers such as hog and boar bristles. The usual method for holding the bristles together and in place within the ferrule consisted of a well-developed art utilizing fluid natural rubber compounded so as to cure to a hard setting when properly heated. Nails or rivets were frequently driven through the ferrule into the hardened rubber and the handle in order to strengthen the brush. It should be noted that the preferred ferrule in the brush making art consists of a bent piece of rust-resisting sheet metal.

In the manufacture of such a typical brush, only a comparatively small amount of rubber enters into its making. Yet its importance can not be too strongly stressed since the success of the brush often depends solely on the bonding material. Two general types of bonding material have been widely used—one consists of a natural rubber cement containing a high percentage of sulphur and usually incorporating a high percentage of fillers. This type of compound often contains much more solvent than solids, requiring a lengthy drying step to remove solvent before curing. The other general type of bristle setting compound in use at present consists of heat-liquefied natural rubber compounded in a similar manner as the rubber cements but requiring no solvent because of the inherent fluidity of the basic rubber derivative used. In both cases the heated compounds are hard and cross-linked and quite different from the so-called vulcanized soft rubbers such as are found in tires and rubber bands.

In the actual manufacture of a brush, the bristle setting compound can be applied either by pouring or dipping. In using the pouring method the bristles are clustered within the ferrule and then inverted. After adjusting the compound to proper viscosity by either thinning or heating, a measured charge of the compound is fed to the bristle containing ferrule. The material penetrates the cluster of bristles to a certain extent while the remainder sets on top and forms a mass which contacts the interior surface of the ferrule. A certain amount of time is allowed for adequate penetration and the poured setting is then allowed to dry for about twenty-four hours. The drying step is required only where there is solvent. After drying, which is often done with low heat, the bristle setting is vulcanized to a hard setting by exposing to a temperature and for a time dependent on the compounding ingredients.

The dipping method is often preferred because of easier penetration, but is usually a slower operation. In dipping the brushes are flax-seeded so that the ferrules can be pushed up out of the way during the dipping process without danger of the brush losing its shape or falling apart during the handling. Wood strips that are often inserted to get proper arrangements of bristles are usually either removed or raised above the dipping compound. The assembly is inserted with the ferrule side down but with the ferrule above the compound. After sufficient penetration the dipped brushes are allowed to drain off the excess compound. Drying and vulcanization are carried out in a similar manner to the pouring process.

In general, the principal problems that arise in the making of a brush deal with poor bonding of the material to the bristles, the cracking of the setting due to shrinkage, separation of materials due to incompatibility, and inadequate penetration with subsequent loosening of bristles. With natural bristles, heat-liquefied natural rubber compounds of high sulphur content, when their fluidity is controlled by proper heating, have been shown to obviate most of these problems.

However, with the recent introduction of synthetic bristles, such as polyamides (e.g. nylon) and polyvinylidene chlorides (e.g. saran), with their superior strength, tenacity, flexibility, wear resistance, water-resistance and solvent resistance, the brush making art has been forced to seek new materials for brush setting compounds. It was early shown that cured natural rubber does not have sufficient adhesion for the synthetic fibers. Further, compounds based on heat-liquefied natural rubber or GR–S synthetic rubber are also unsatisfactory for use with synthetic bristles. Various other synthetic rubbers and resins have been tried but have been found unsatisfactory either because of poor bonding, incompatibility of the components or shrinking.

Thus, heat-liquefied natural rubber forms a homogeneous setting with synthetic bristles but bonds poorly to the bristles. Phenol-aldehyde resins are known to have good bonding affinity for many synthetics. So, attempts have been made to incorporate phenolic resins into heat-liquefied natural rubber. These attempts have failed because of the incompatibility of phenol-aldehyde resins with such heat liquefied rubber. The incompatibility shows itself in separation and stratification of the two principal ingredients, so that when used on a brush the setting is even poorer than before.

When phenol-aldehyde resins are blended with compatible compounds, the resultant materials have improved bonding qualities but demonstrate structural instability. Thus, blends of phenolic resins with rubbery copolymers of butadiene and acrylonitrile are compatible and show excellent adhesion in other applications. However, when used as a bristle setting there results a severe shrinkage and cracking, with separation of bristle clumps, even though there is satisfactory bonding of the compound to the bristles.

It can be seen, therefore, that a satisfactory bristle setting compound must have many properties other than those usually associated with adhesives. A satisfactory bristle setting compound must be fluid, smooth and uniform. It must not contain incompatible ingredients which would separate out either before or after curing. It should be stable and should be amenable to viscosity control, inasmuch as the appropriate viscosity for a particular application is often governed by other factors. Further, a satisfactory brush setting compound must be curable by heat to a hard rigid mass, quite unlike ordinary rubber-base adhesives which cure to soft elastic products. In addition a bristle setting compound should

have a good initial grip on fibers and should be capable of penetrating and filling in spaces between the individual bristles. After the bristles setting compound has been applied, there should be little, if any, delay in production occasioned by a long drying step. After heat curing the final bond should be tight and hard, and the mass of compound should be cohesive. A satisfactory brush setting compound, after curing, should evidence no shrinking or cracking, and no separation of either bristles from the mass or portions of the mass from other portions of the mass. All of these characteristics are required by the present market and technique of brush making. If satisfactory synthetic bristle brushes are to be made, materials containing all the above qualities are necessary in order to use the present simple brush-making method which, other than a metering device for delivering quantities of the material and a heating device for obtaining a cure, requires no special or unusual equipment.

The present invention provides compounds which meet the above-stated requirements for satisfactory bristle setting materials, can be used with both natural and synthetic bristles and can be formulated either with no solvent or with only a small percentage of solvent. In accordance with this invention, we prepare compatible blends containing substantial portions of fusible, thermo-setting phenol-aldehyde resins and liquid, low-molecular weight copolymers of conjugated diolefins of 4 to 6 carbon atoms with acrylonitrile and substituted acrylonitriles. The preferred proportions are 20 to 400 parts of resin per 100 parts of liquid copolymer. Common compounding ingredients such as sulphur, fillers and accelerators of vulcanization for unsaturated copolymers (hereinafter referred to as "co-polymer accelerators") are desirable but not essential for the practice of this invention. The compounds may be used as such or may be dissolved in a small amount of solvent before using.

We prefer that the liquid copolymers have an acrylonitrile or substituted acrylonitrile content of from 15 to 45 percent and a viscosity of less than two million centipoises as measured by a Brookfield electric viscometer at 10 revolutions per minute with a number 2 spindle at 25° C. It is also preferred that the liquid copolymer be substantially completely converted and have little monomer content.

Practically any fusible thermo-setting phenol-aldehyde resin can be used, including as phenol components: phenol, cresol, xylenol, naphthol, resorcinol, cardanols, cashew nut shell oil, modified cashew nut shell oil, other substituted phenols and mixtures thereof. The aldehyde component can be any aldehyde reactive with the phenol, including formaldehyde, acetaldehyde, furfural, or polymers, addition products and mixtures thereof. It should be clearly understood that any phenol-aldehyde resin which is fusible and thermo setting can be used.

Liquid copolymers for use in this invention can be prepared by copolymerising acrylonitrile or a substituted acrylonitrile such as alphamethacrylonitrile, alpha-ethacrylonitrile or alpha-chloracrylonitrile with a conjugated diolefin of 4 to 6 carbon atoms such as butadiene-1,3, isoprene or dimethyl butadiene. Such copolymers are preparable in emulsion at slightly elevated temperatures and in the presence of an oxygen-yielding catalyst such as hydrogen peroxide, benzoyl peroxide, potassium persulfate or other alkaline metal persulfates or perborates or mixtures thereof. When the monomers are converted to 70% or over in the presence of small amounts of modifiers such as .5 to 2 percent of alkyl mercaptans containing 6 to 16 carbon atoms, the coagulated products are elastomeric solids. However, by using large amounts of such modifiers (i. e. 3–12%), the product upon coagulation is a normally liquid, non-rubbery, low-molecular weight copolymer resembling a viscous oil. These viscous, oily copolymers have viscosity-average molecular weights typically below 15,000, and viscosities of less than two million centipoises as measured by a Brookfield electric viscometer at 25° C. with number 2 spindle.

A useful general formulation for preparing such liquid copolymers is as follows:

	Parts
Conjugated diolefin	85 to 55
Acrylonitrile or substituted acrylonitriles	15 to 45
Fatty acid soap	4
Alkyl mercaptan	6
Potassium persulfate	0.3
Water	200

The agitated mixture is treated for 15 to 20 hours at 20° C., which leaves little unreacted monomer, and the latex is then stabilized by addition of a small amount of ditertiary butaparacresol. The stabilized latex is then coagulated with brine, washed with alcohol and water, and dried at 125° C., to give the oily, non-rubbery copolymer.

The phenol aldehyde resins usable in this invention are those which are of the so-called A or B stage, i. e. those substantially free of cross-linking but reactive with a methylene releasing agent, such as hexamethylene tetramine, to yield cross-linked compounds. These phenolic resins are usually prepared by the condensation of a phenol with an aldehyde, the reaction being stopped at such a point that the resin is still fusible and soluble in polar solvents. In addition, the resin may be either a straight phenol-aldehyde resin or such a resin as modified according to known practice.

In particular, we prefer, to use in this invention, a mixture of ordinary phenol and cardanol as the phenol component of the resin. Cardanol is commonly obtained from the heating of cashew nut shell oil. These resins are commonly known as "cashew nut shell oil-modified phenolaldehyde resins." A typical formulation is as follows:

9.5 mols phenol
0.5 mols cardanol
8.0 mols formaldehyde
0.12 mols aqueous hydrochloric acid

wherein the mixture is heated for three hours at 95° C. and the water removed at reduced pressure.

For the purposes of this invention base-catalyzed resins known as "resoles" have an equivalent use to the acid-catalyzed or "novolak" resins. It is to be understood that the condensation of the phenolic resins for use in this invention must not be carried beyond the fusible stage before incorporation with the liquid copolymer.

In the preparation of a bristle setting compound in accordance with this invention we have found that the following general formulation is extremely useful:

Liquid diene-nitrile copolymer	80 to 100 parts.
Phenol-aldehyde resin	20 to 400 parts.
Phenolic resin hardening agent	0 to 10% of resin.
Sulphur	0 to 50 parts.
Copolymer accelerator	0 to 5 parts.
Filler	0 to 500 parts.

Examples of common fillers are barytes, carbon black and clay. An example of copolymer accelerators is the condensation product of butyraldehyde and aniline. A common resin curing agent is hexamethylene tetramine.

With the foregoing general discussion in mind, there are given herewith specific examples of the practice of this invention wherein all parts given are by weight.

Example 1

A formulation satisfactory for dipping or pouring of the brush-setting compound is prepared as follows:

First, a liquid copolymer of butadiene and acrylonitrile is prepared using the following ingredients:

	Parts
Butadiene	70
Acrylonitrile	30
Sodium oleate	4
Lauryl mercaptan	6
Potassium persulfate	0.3
Water	200

The above ingredients are mixed together and allowed to react at a temperature of 30° C. for 15 hours, with constant agitation. The resultant latex is then stabilized by addition of 1 part of ditertiary butaparacresol. After stabilization the latex is coagulated with brine to give an oily viscous liquid. This is washed with alcohol and water and then dried at 125° C. The viscosity of this viscous, liquid polymer is approximately 175,000 centipoises at 75° F., with a viscosity-average molecular weight range of from 3,000 to 6,000. This material is referred to in remainder of this example as "liquid copolymer".

A fusible phenolic resin is then prepared by heating 10 mols of phenol with 8 mols of formaldehyde in the presence of 0.12 mols of hydrochloric acid for a period of 3 hours at 95° C. After the reaction is complete, the resin is dried by the boiling off of the water at reduced pressure. This material is referred to in the remainder of the example as "phenolic resin".

To prepare the brush-setting compound in accordance with this invention, the liquid polymer and phenolic resin are compounded as follows:

	Parts
Liquid copolymer	100
Sulphur	45
Barytes	150
Condensation product of butyraldehyde and aniline	2
Zinc oxide	5
Calcium oxide	10
Phenolic resin	150
Methyl isobutyl ketone	75
Hexamethylene tetramine	12

In mixing the resin and liquid copolymer, the preferred apparatus is an internal mixer containing either dispersion or sigma blades and equipped with a jacket for temperature control. After the dry ingredients are well dispersed the solvent is then slowly added and agitated until a uniform product is obtained. The compound can be modified by small additions of either powdered or milled rubbery copolymers so as to modify the penetration characteristics. In standard brush pouring equipment, the compound can be heated to the range 160 to 200° F. to obtain proper viscosity for satisfactory penetration.

After the compound has been applied by either dipping or pouring, the setting is placed in a circulating air oven for a period of 4 hours at 150° F. to remove most of the solvent. The complete brush assembly can then be cured by heating at 295° F. for 4½ hours. Examination of settings made with natural, nylon and saran bristles all showed settings free of shrinkage and splits.

In each case, the full strength of the fingers was unable to separate a bristle clump without tearing the bristles. The settings were structurally homogeneous, whether made by dipping or pouring and, further, showed no signs of separation between the copolymer and resinous phases either before or after the heat curing step. It was found that brushes made with setting compounds substituting either natural rubber, heat liquefied natural rubber, neoprene, GR–S, or rubbery copolymer of butadiene-acrylonitrile for the liquid copolymer, or for both the liquid copolymer and the resin, showed severe cracking due to shrinkage and had bristles which were released from the setting in clusters upon low pull of the fingers.

Example 2

The liquid copolymer for this example was prepared in a similar manner to that of Example 1, except that a molal ratio of 75 parts of butadiene was used per 25 parts of acrylonitrile. The phenolic resin used in this example was prepared in a manner similar to Example 1, except that in place of 12 mols of phenol a mixture consisting of 11.0 mols of phenol and 1.0 mol of cardanol was used. The liquid copolymer and phenolic resin were compounded as follows:

	Parts
Liquid copolymer	100
Sulphur	45
Barytes	150
Butyraldehyde-aniline	2
Zinc oxide	5
Calcium oxide	10
Phenolic resin	100
Hexamethylene tetramine	6

The ingredients were well mixed and dispersed in a heavy duty internal mixer, to give a viscous flowable brush compound. When either poured or dipped, as in the previous example, exceedingly strong brushes were formed in which the bristles could not be removed from the setting without breaking the bristles.

With both Examples 1 and 2, all the brushes made were free of splits. These compounds were found to be as effective with nylon as with animal hair bristles and, further, bonded well to the ferrule. There were no signs of separation in the compound itself or in the setting between the rubber and resinous phases. When either of the compounds of Examples 1 and 2 were poured on to the butt end of bristles within a ferrule and then cured in a similar manner, comparable high strength brushes were obtained. A striking advantage of Example 2 compound is that the solvent drying step is completely eliminated. It should be noted that while Example 1 has solvent, its percentage solids is approximately 80 percent as compared to a maximum practical solids concentration of 40 percent with normally solid elastomers.

It should be noted that although, as in Examples 1 and 2, a high percentage sulphur is utilized, that such sulphur is not necessary. Sulphur is normally used in these proportions to form a cross-linked compound. In this case, the cross-linking can be provided by the resin alone. Likewise the copolymer accelerator may be omitted if the sulphur is omitted. However, the presence of both sulphur and accelerator does tend to give excellent hard settings.

Inasmuch as thermo-setting phenol aldehyde settings can be prepared in a variety of ways, it is not always necessary to add a separate hardening agent. The resin as prepared may or may not contain sufficient hardening ingredients. If it does not, a hardening ingredient should be provided. In the appended claims we mean the term "thermo-setting phenol-aldehyde resin" or "thermo-setting condensation product" to include the required amount of hardening agent which would normally react with the resin upon heating to form a hard infusible resin.

We claim:

1. A brush having its bristles embedded in a setting which is substantially free of splits and shrinkage cracks and which is bonded firmly to a surrounding ferrule; said setting being the heat-hardened product of a fluid composition containing as a major ingredient a blend of a fusible thermo-setting phenol-aldehyde resin and a normally liquid non-rubbery copolymer of a member of the group consisting of acrylonitrile and alpha alkyl substituted acrylonitrile with a conjugated diene having 4 to 6 carbon atoms; said copolymer having a viscosity of less than 2,000,000 centipoises at 25° C.

2. Claim 1 wherein the bristles are selected from the group consisting of nylon and saran.

3. Bristles embedded in the heat-hardened blend of a fusible, thermosetting phenol-aldehyde resin and a normally liquid non-rubbery copolymer of a conjugated diene having 4 to 6 carbon atoms with a member of the group consisting of acrylonitrile and alpha alkyl substituted acrylonitrile; said copolymer having a viscosity at 25° C. of less than 2,000,000 centipoises.

4. Claim 3 wherein the bristles are selected from the group consisting of nylon and saran.

References Cited in the file of this patent

UNITED STATES PATENTS

2,410,079	Kellgren	Oct. 29, 1946
2,469,132	Schulze et al.	May 3, 1949
2,508,908	Enchelmaier	May 23, 1950
2,521,361	Gessler	Sept. 5, 1950
2,552,904	Newberg et al.	May 15, 1951
2,638,460	Crouch	May 12, 1953
2,647,019	Maynard	July 28, 1953
2,725,981	Abere et al.	Dec. 6, 1955

FOREIGN PATENTS

953,239	France	May 16, 1949