Aug. 17, 1943. D. R. WIGGAM ET AL 2,326,811

BRUSH COMPRISING PLASTIC MASS

Filed March 30, 1940

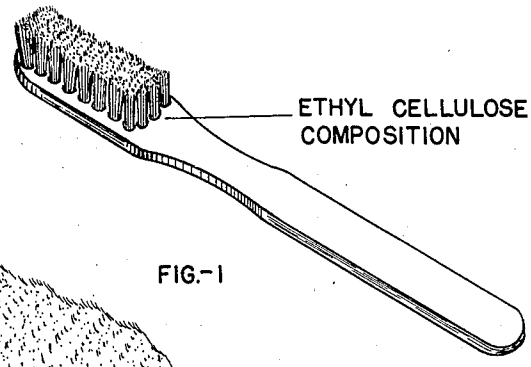

FIG.-1

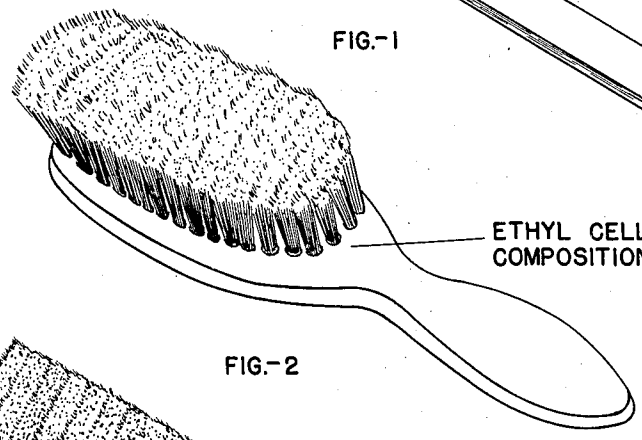

FIG.-2

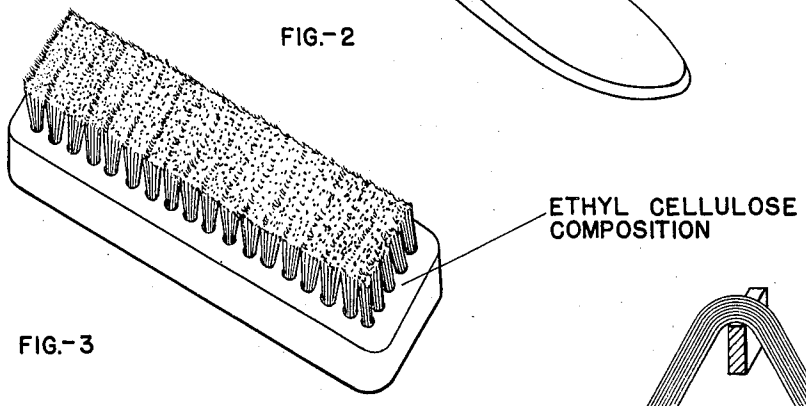

FIG.-3

FIG.-4

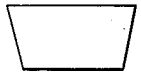

FIG.-5



FIG.-5A

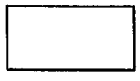

FIG.-6



FIG.-6A

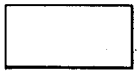

FIG.-7



FIG.-7A

DAVID R. WIGGAM &
WILLIAM KOCH
INVENTOR.

BY Cleveland B. Hollaway Jr.

Patented Aug. 17, 1943

2,326,811

UNITED STATES PATENT OFFICE

2,326,811

BRUSH COMPRISING PLASTIC MASS

David R. Wiggam, West Grove, Pa., and William Koch, Wilmington, Del., assignors to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

Application March 30, 1940, Serial No. 326,832

8 Claims. (Cl. 15—159)

This invention relates to brushes of the type in which bristle tufts are mounted in a plastic mass. More particularly, it relates to toothbrushes, hair brushes, clothes brushes, and other brushes which it may be found desirable to sterilize.

Brushes consisting of bristle tufts mounted in plastic masses are particularly attractive in appearance and hence this type of construction is used for toothbrushes, hair brushes, etc. Such brushes must be capable of sterilization without loosening of the bristles. Heretofore, sterilizable brushes of this type have been based upon the use of nitrocellulose plastics such as Celluloid. Nitrocellulose is highly inflammable and its use in manufacturing operations and storage is subject to many restrictions for this reason.

Less flammable materials of strength, appearance and toughness similar to nitrocellulose plastics have not been used to support brush bristles as no plastics of this type which do not warp under the conditions of heat and moisture utilized in sterilization have been known. Loosening and loss of bristles as a result of sterilization have rendered known materials impractical for the purpose.

It is an object of this invention to provide sterilizable brushes containing only materials which are not highly flammable.

It is a further object to provide sterilizable brushes which will not warp with consequent loosening or loss of bristles under the ordinary conditions of use or under the conditions of periodic sterilization.

It is a still further object to provide sterilizable brushes which are resistant to permanent deformation under the stress of use.

It is a still further object to provide brushes, the plastic of which does not become soft or sticky, when subjected to hot water.

It is a still further object to provide brushes, the plastic of which is resistant to soaps and other mild alkalies and acids encountered in ordinary use.

In the drawing:

Figure 1 illustrates a toothbrush in accordance with this invention.

Figure 2 illustrates a hair brush in accordance with this invention.

Figure 3 illustrates a brush in accordance with this invention intended for miscellaneous general use.

Figure 4 illustrates a bristle tuft of the folded type.

Figures 5, 6, and 7 illustrate tuft anchors in side view; Figures 5*a*, 6*a*, and 7*a* are end views respectively thereof.

Now in accordance with this invention the objects mentioned are attained by mounting bristle tufts in a plastic mass consisting of an ethyl cellulose composition characterized by permanent rigidity at a sterilizing temperature.

The plastic composition utilized in making the brushes of this invention is based upon ethyl cellulose of the type which has an ethoxyl content in the range between about 41% and about 51% and preferably in the range between about 44% and about 48%. The viscosity characteristic of the ethyl cellulose determined as hereinafter specified will have a value above about 50 centipoises and preferably will lie in the range between about 70 and about 300 centipoises.

To obtain a plastic capable of withstanding the conditions of hot water sterilization without loosening of bristles, it is desirable that the plastic utilized have a relatively high content of ethyl cellulose. The plastic will comprise in general at least about 70% ethyl cellulose. It may, in fact, consist entirely of ethyl cellulose. However, for nearly all purposes, the plastic utilized in the brushes according to this invention will comprise a resinous substance to give a readily moldable water resistant composition. In addition, a

toughening or softening or plasticizing modifier may be included. Molding lubricants, solid fillers, and coloring matter represent additional ingredients which are optional.

The resin in general utilized in the plastic imparts to the ethyl cellulose composition resistance to hot water and the ability to be readily worked. The quantity of resin will be not more than about 25% of the plastic and preferably will lie in the range between about 5% and about 20% of the plastic. The incorporation of the resin in the plastic within the range specified improves the molding characteristics of the material. This improvement in molding characteristics is especially valuable when brush blanks or the brushes themselves are prepared by injection molding. Desirably, only resins which are insensitive to water are utilized. Preferably, resins which are low in color and stable in color are utilized but there will be many cases in which a dark color is of no consequence. Resins such as, for example, cumarone resin, glyceryl ester of rosin or of hydrogenated rosin, erythritol or pentaerythritol ester of rosin or hydrogenated rosin, modified phenolic resin, manilla gum, dammar gum, hydrogenated rosin, oil soluble phenolic resins, substantially petroleum hydrocarbon insoluble pine wood resin, rosin modified alkyd resins, rosin modified glyceryl maleate, urea formaldehyde resin, sorbitol rosin ester or sorbitol hydrogenated rosin ester, glyceryl ester of hydrogenated rosin modified with alkyd resin, etc. are suitable.

The modifier, or mixture of modifiers, which may be included in the ethyl cellulose plastic to toughen, soften, plasticize, or otherwise improve the plastic, will in no case exceed more than about 20% of the plastic composition. Preferably, the modifier or mixture of modifiers will comprise between about 5% and about 15% of the plastic. Modifier or modifiers used must be insoluble in water and resistant to the action of water; preferably the modifier will be water repellent in nature. Preferably, chlorinated diphenyl, methyl phthallyl ethyl glycollate, dibutyl phthalate, ethyl ortho-benzoyl benzoate or refined mineral oil is used in the brushes of this invention. The refined mineral oil is any substantially non-volatile liquid petroleum, cracked petroleum, or hydrogenated petroleum fraction. Desirably, of course, a colorless, odorless product is utilized. The mineral oil serves as a cheapening liquid filler which improves moldability, toughness, and resistance of the plastic slightly without much softening action in moderate quantities. The other modifying materials mentioned are softeners or plasticizers having the effect of softening and toughening the plastic and lowering its molding temperature. Other modifiers such as castor oil, hydrogenated methyl abietate, polyhydric alcohol esters of sebacic and homologous acids, oil extended alkyd resins, triphenyl phosphate, tributyl aconitate, tricresyl phosphate, etc. may be utilized instead of or with the preferred modifiers mentioned. However, it is desirable that the modifier utilized impart no greater water sensitivity than ethyl ortho-benzoyl benzoate to the ethyl cellulose plastic.

The plastic utilized in the brushes of this invention may also comprise a small quantity of a molding lubricant which may be a waxy or soapy substance. Paraffin wax, ceresin, montan wax, Japan wax, carnauba wax, zinc stearate, magnesium stearate, aluminum stearate, aluminum palmitate, etc. are, for example, suitable. These materials will be used in quantity which is insufficient to impart greasiness to the plastic or which will detract unduly from its strength and appearance. Where a lubricant is used, its quantity will be no more than about 5% and preferably, where used, the lubricant will be in quantity between 0.5% and about 2% of the plastic. A molding lubricant insures good mold release in preparing the brushes.

The plastic may also contain dyestuffs and fillers. Dyestuffs of the oil soluble and alcohol soluble type stable to processing temperatures are suitable. They are used in very small quantities. Pigments and other solid fillers may be used if desired in quantities insufficient to impart brittleness or poor molding characteristics to the plastic. Where utilized at all they will rarely exceed about 5% of the plastic and in most cases will be used in a quantity less than about 2% of the plastic. It will be understood that where the plastic or a percentage of the plastic is referred to herein and in the claims, the percentages will refer to the plastic ingredients not including solid fillers as 100%. Pigments and fillers have value only in contributing to the appearance of the plastic.

The plastic masses utilized to support the bristle tufts in accordance with this invention may be prepared by the Celluloid process. This method is desirably utilized when the plastic consists entirely or almost entirely of ethyl cellulose with little or no toughener or resin to aid colloiding.

The compositions of this invention may be advantageously prepared entirely without the use of volatile solvents. For example, the ingredients of the composition may be mixed in lump or powder form and colloided in a suitably heated Banbury mill. The ingredients are charged into the heated mill and colloided in the usual manner, except, it is to be noted, no volatile solvents are used. The colloided mass is removed from the Banbury mill and rolled into a sheet while still hot. The sheet is broken up and reduced to the usual form of coarsely granulated or more or less pulverulent molding powders by means of a rotating knife mill, hammer mill, or other suitable reducing means.

A typical procedure for compounding the molding powder ingredients in the Banbury mill is to mix the ingredients roughly and add them to the Banbury mill which is maintained at a temperature of the order of about 280 to about 330° F. Pressure is applied to the floating plug and the mass is mixed until it is homogeneous. A mixing period between about 8 and about 15 minutes is usually sufficient. If desired, the rotors and the jacket of the mill are cooled slightly at the end of the homogenizing period to facilitate discharge from the mill. The hot colloided mass is removed from the Banbury mill and is then immediately sheeted on a hot two roll mill. The sheet is then allowed to cool after which it is reduced to a chipped granular or powdered injection molding powder. This specific procedure is suitable for the composition given in the examples included in this specification.

Alternatively, the ingredients of the molding powder may be colloided by rolling on a suitably heated differential two roll mill of the type well known in the plastic art. In a typical procedure the roughly mixed ingredients are placed on the mill with the two rolls at a temperature of the order of about 280 to about 330° F. Colloiding

occurs rapidly. The mass is cut and worked on the rolls until completely homogeneous. This usually requires about 10 to about 15 minutes. The slower roll is usually then cooled until the plastic mass adheres entirely to the hotter roll. The plastic is then stripped from the mill as a sheet and is reduced to a molding powder when cooled.

The sheet from the two-roll mill may be stamped into pre-forms while still hot, if desired, instead of reducing to a molding powder.

The plastic mass utilized in the preparation of the brushes according to this invention may be formed and shaped by colloiding the ingredients of the plastic composition by heat and mechanical working, reducing the colloided plastic to a molding powder, and then molding this powder by the compression or injection method to form the plastic mass. Alternatively, the molding powder or colloided plastic may be formed into rods, strips, sheets, etc. which may then be further shaped to plastic brush blanks by hot pressing or stamping.

A particular advantage of this invention lies in the preferred method of shaping the plastic brush mass by injection molding using the colloided plastic in the molding powder form. The compositions which contain a resin in the preferred quantity hereinbefore given and especially the compositions which contain both a resin and a modifier in the preferred ranges hereinbefore given are most suitable for shaping of the plastic by injection molding. The usual commercially available injection molding presses may be utilized. The temperature and pressure required for injection of the particular composition used will readily be found by trial. The compositions herein described usually inject well at temperatures between about 350° F. and about 400° F. at pressures between about 800 and about 2,000 lbs./sq. inch.

After the plastic mass has been molded to a suitable shape, bristle-sockets are drilled in the usual manner. Alternatively, the bristle sockets are molded while the plastic is being shaped. This latter procedure is especially convenient and furnishes an advantage when injection molding is utilized as the shaping procedure. Bristle tufts are formed in the usual manner and are pressed into the tuft sockets. Preferably, a folded tuft construction is used, for example, of the type shown in Figure 4. Desirably, a metal wedge or anchor such as, for example, the wedge or anchor described in U. S. Patents 449,344; 1,879,103; 1,972,691 and the like are used to aid in fastening the bristles. Further examples of anchors which may be utilized are shown in Figures 5, 6, and 7. Figures 5*a*, 6*a*, and 7*a* are end views of anchors, side views of which are shown in Figures 5, 6, and 7, respectively. Alternatively, or in addition to a bristle anchor, the bristle tuft may be held in place by staking or swaging the plastic composition about the opening of the bristle tuft socket as shown in U. S. Patent 1,919,011.

In an alternative method for preparing the brushes in accordance with this invention, ethyl cellulose molding plastic of the type described hereinbefore and in the examples given subsequently as suitable for the injection molding process is shaped about bristle tufts positioned in the mold by injection molding, whereby the plastic mass is shaped and the bristles are mounted therein in a single operation. Preformed bristle tufts of either the folded or unfolded type are placed in the injection mold and the molten plastic is forced into the mold. Preferably, a folded tuft construction utilizing a metal anchor of the type hereinbefore referred to is utilized. A remarkably permanent article is produced by this method.

In the drawing, Figures 1, 2, and 3 illustrate three shapes of brush for which the method of this invention is particularly suitable. However, the invention is not limited to any particular shape or to any particular use for the brush.

The examples in Tables I to IV inclusive give compositions suitable for the plastic portion of the brushes in accordance with this invention. In the examples and in the specification and claims all parts and percentages are by weight.

Examples 23 to 27 inclusive illustrate compositions preferably shaped by the Celluloid process although they may be injection molded. The remaining examples illustrate compositions particularly suitable for the injection molding method of shaping the plastic.

TABLE I

	Example No.												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Ethyl cellulose (47.5% ethoxyl) (viscosity 93)	75	75	75	75	75	75	75	75	75	75	75	75	75
Clear, colorless mineral oil (Fractol A)	5	5	5	5	5	5	5	5	5	5	5	5	5
Chlorinated diphenyl (Aroclor 1260)	5	5	5	5	5	5	5	5	--	--	--	--	--
Ethyl ortho-benzoyl benzoate (Ketonone E)	--	--	--	--	--	--	--	--	5	5	5	5	5
Japan wax	2	2	2	2	2	2	2	2	2	2	2	2	2
Sorbitol ester resin (Atlas Resin 311-B)	15	--	--	--	--	--	--	--	15	--	--	--	--
Oil soluble phenolic resin (Durez 550)	--	15	--	--	--	--	--	--	--	15	--	--	--
Batavia dammar	--	--	15	--	--	--	--	--	--	--	15	--	--
Cumarone resin (Neville R-29)	--	--	--	15	--	--	--	--	--	--	--	15	--
Rosin modified terpene-maleic anhydride resin (Petrex 1)	--	--	--	--	15	--	--	--	--	--	--	--	15
Hydrogenated rosin	--	--	--	--	--	15	--	--	--	--	--	--	--
Oil soluble phenolic resin (Super-Beckacite 2000)	--	--	--	--	--	--	15	--	--	--	--	--	--
Petroleum hydrocarbon insoluble pine wood resin	--	--	--	--	--	--	--	15	--	--	--	--	--

TABLE I (Cont.)

	Example No.		
	14	15	16
Ethyl cellulose (47.5% ethoxyl) (viscosity 93)	75	75	75
Clear, colorless mineral oil (Fractol A)	5	5	5
Ethyl ortho-benzoyl benzoate (Ketonone E)	5	5	5
Japan wax	2	2	2
Hydrogenated rosin	15	--	--
Oil soluble phenolic resin (Super-Beckacite 2000)	--	15	--
Petroleum hydrocarbon insoluble pine wood resin	--	--	15

TABLE II

Ethyl cellulose brush plastics

	Example No.					
	17	18	19	20	21	22
Ethyl cellulose (47.5% ethoxyl) (viscosity 93)	75	75	70	--	--	--
Ethyl cellulose (47.8% ethoxyl) (viscosity 90.9)	--	--	--	75	--	--
Ethyl cellulose (44.6% ethoxyl) (viscosity 158)	--	--	--	--	80	--
Ethyl cellulose (44.6% ethoxyl) (viscosity 125)	--	--	--	--	--	80
Clear, colorless mineral oil (Fractol A)	10	--	5	10	7.5	7.5
Chlorinated diphenyl (Aroclor 1260)	--	10	5	--	--	--
Rosin modified terpene maleic anhydride resin (Petrex 1)	15	15	20	--	--	--
Batavia dammar	--	--	--	15	12.5	--
Glycerol ester of hydrogenated rosin containing 10% by weight of glyceryl ester of maleic acid	--	--	--	--	--	12.5
Japan wax	2	2	2	2	2	2

TABLE III

	Example No.				
	23	24	25	26	27
Ethyl cellulose [1]	150.0	-----	142.5	-----	135.0
Ethyl cellulose	-----	150.0	-----	142.5	-----
Dibutyl phthalate	-----	-----	-----	-----	3.75
Refined mineral oil (Fractol A)	-----	-----	-----	-----	3.75
Glyceryl ester of hydrogenated rosin containing 10% by weight of the glyceryl ester of dibasic acid	-----	-----	7.5	7.5	7.5

[1] 44.4% ethoxyl, 85 centipoises in 5% solution of the ethyl cellulose in a solvent composed of 70% toluene and 30% 2-B alcohol by weight

TABLE IV

Ethyl cellulose brush plastics colored by pigments and dyes

	Example No.					
	28	29	30	31	32	33
Ethyl cellulose (ethoxyl 44.1%) (viscosity 109)	120	120	120	120	120	120
Hydrogenated rosin glycerol ester	18.75	18.75	18.75	18.75	18.75	18.75
Fractol A	11.25	11.25	11.25	11.25	11.25	11.25
Japan wax	3.0	3.0	3.0	3.0	3.0	3.0
Oil soluble yellow (Calco)	0.042	-----	0.015	-----	-----	-----
Oil soluble red (Calco)	0.028	-----	-----	-----	-----	-----
Oil soluble green (Calco)	-----	0.007	-----	-----	-----	-----
Oil soluble blue (Calco)	-----	-----	-----	0.008	-----	-----
Ulrich Cadmium Yellow No. 1133	-----	-----	-----	-----	0.080	2.00
TiO_2	0.030	0.060	0.090	0.115	-----	-----

Brushes prepared using the plastic compositions illustrated by the examples are substantially non-inflammable. At most, they can just support combustion. In no case do they exhibit the violent rapid burning characteristic of Celluloid articles. Furthermore, the brushes are tough and durable. They stand very well the stresses of use and sterilization and are resistant to the action of mild acids and alkalies.

One of their outstanding characteristics is their ability to resist water. Plastics according to the examples given herein in most cases absorb only between about 2 and about 4% of their own weight of water upon immersion for one week at room temperatures. In this respect the plastic utilized is at least equal to and in some cases somewhat better than Celluloid brush plastics which usually absorb above 3% of water by the same test. The brushes according to this invention are characterized by their ability to withstand repeated sterilization by hot water such as water at a temperature of 180° F. and in many cases at higher temperatures without appreciable warping and without loss or loosening of the bristles, i. e. both the finished brush and the plastic or plastic mass of the brush are substantially unaffected by hot water.

The term "viscosity characteristic" used herein in describing the ethyl cellulose used according to this invention refers to the viscosity in centipoises at 25° C. of a solution consisting of 5% by weight of the ethyl cellulose in question and 95% by weight of a solvent which in turn consists of 70% by weight of toluene and 30% by weight of ethyl alcohol.

It will be understood that the details and examples hereinbefore set forth are illustrative only and that the invention as broadly described and claimed is in no way limited thereby.

What we claim and desire to protect by Letters Patent is:

1. A brush comprising, in combination, a plastic mass substantially unaffected by hot water comprising:

	Percent
Ethyl cellulose having an ethoxyl content between about 41% and about 51%	In excess of about 70
Substantially non-volatile liquid refined mineral oil	About 5 to about 20
A water resistant softening modifier miscible with said oil	About 5 to about 20

and a bristle tuft mounted in said plastic mass.

2. A brush comprising, in combination, a plastic mass substantially unaffected by hot water comprising:

	Percent
Ethyl cellulose having an ethoxyl content between about 41% and about 51%	In excess of about 70
A water resistant resin compatible with said ethyl cellulose	About 5 to about 15
Substantially non-volatile liquid refined mineral oil	About 5 to about 15
A water resistant softening modifier miscible with said oil	About 5 to about 15

and a bristle tuft mounted in said plastic mass.

3. A brush consisting of a plurality of bristle tufts mounted in a plastic mass consisting of:

	Percent
Ethyl cellulose having an ethoxyl content between about 44% and about 48%	About 73
Substantially non-volatile liquid refined mineral oil	About 10
Rosin modified alkyd resin derived from polyhydric alcohol and terpene-maleic anhydride condensation products	About 15
Japan wax	About 2

4. A brush consisting of a plurality of bristle tufts mounted in a plastic mass consisting of:

	Percent
Ethyl cellulose having an ethoxyl content between about 44% and about 48%	About 73
Substantially non-voltaile liquid refined mineral oil	About 10
Dammar gum	About 15
Japan wax	About 2

5. A brush consisting of a plurality of bristle tufts mounted in a plastic mass consisting of:

	Percent
Ethyl cellulose having an ethoxyl content between about 44% and about 48%	About 78
Substantially non-volatile liquid refined mineral oil	About 7.5
Glycerol ester of hydrogenated rosin	About 12.5
Japan wax	About 2

6. A brush comprising, in combination, a plastic mass substantially unaffected by hot water comprising:

	Percent
Ethyl cellulose having an ethoxyl content between about 41% and about 51%	In excess of about 70
Rosin modified alkyd resin derived from polyhydric alcohol and terpene-maleic anhydride condensation products	About 5 to about 15

	Percent
Substantially non-volatile liquid refined mineral oil	About 5 to about 15
A water resistant softening modifier miscible with said oil	About 5 to about 15

and a bristle tuft mounted in said plastic mass.

7. A brush comprising, in combination, a plastic mass substantially unaffected by hot water comprising:

	Percent
Ethyl cellulose having an ethoxyl content between about 41% and about 51%	In excess of about 70
Dammar gum	About 5 to about 15
Substantially non-volatile liquid refined mineral oil	About 5 to about 15
A water resistant softening modifier miscible with said oil	About 5 to about 15

and a bristle tuft mounted in said plastic mass.

8. A brush comprising, in combination, a plastic mass substantially unaffected by hot water comprising:

	Percent
Ethyl cellulose having an ethoxyl content between about 41% and about 51%	In excess of about 70
Glycerol ester of hydrogenated rosin	About 5 to about 15
Substantially non-volatile liquid refined mineral oil	About 5 to about 15
A water resistant softening modifier miscible with said oil	About 5 to about 15

and a bristle tuft mounted in said plastic mass.

DAVID R. WIGGAM.
WILLIAM KOCH.