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PREPARATION OF A SULFOMETHYLATED BISPHENOL-FORMALDEHYDE COMPOSITION FOR TREATING WOOL

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This invention relates to methods and compositions for reducing felting and shrinking of wool and other animal hair fibers and to the novel shrink resistant animal hair fiber products so-produced. Other aspects of this invention are concerned with new techniques for producing sulfomethylated condensation products of bisphenols and aldehydes and to the products so-produced.

Felting shrinkage of animal fiber textiles during wet mechanical processes such as dyeing and laundering has long been a major disadvantage of wool and other animal hair fibers. Without some non-felting or "shrink-resist" treatment, the wool material becomes so dense and compact that reduction in area causes it to be unusable. Furthermore, the compacted nature of the felted material is such that there is loss of elasticity of the fabric and the material is difficult to penetrate or clean.

Currently, it is thought that certain directional friction properties of the fibers, in addition to the ability to stretch and to recover from stretching, are the primary causes of the felting which occurs when a woolen fabric is subjected to repeated stresses in the wet.

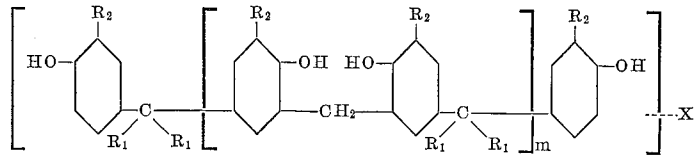
A considerable amount of research work in the past has produced a great variety of methods and techniques aimed at solving the problem. These methods have been based on various reactions which modify the surface of the wool fiber, alter the elastic properties of the fiber, or act by a combination of these mechanisms. Chemical treatments have involved chlorination, oxidation, reduction, alkaline hydrolysis, enzyme degradation, resin application, and polymerization on or in the fiber. Certain of these treatments are degradative and therefore require careful control to prevent excessive damage to the fibers. Others require special equipment, solvents, expensive reagents, are hazardous to use, etc. The additive treatments, employing resins and polymers also have certain problems associated with their use. Many of the treatments can only be used on wool fabrics—other wool forms cannot be effectively processed. Some known treatments cause loss of wool-like hand when too much resin is added on. It has been indicated recently that in the cases of silicones and polyamide-polyepoxides shrinkage control is obtained only at the expense of increased fabric stiffness.

The desired result is attained in many of these methods only at the expense of wool quality, as shown by weight loss, yellowing, harsh hand, increased luster and decreased durability. Generally speaking, there is as yet no completely satisfactory method available for making

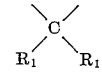
animal hair fiber products shrink-proof. In addition, we are not aware of any successful method for shrink-proofing wool involving incorporation of a substantive (to wool) water-soluble condensation product directly in the dye bath or in the laundry wash liquor. It seems desirable to be able to dye, launder, or otherwise wet process woolens in a manner similar to that used presently for cottons, rayons, and synthetics, without the usual felting which has heretofore accompanied such wet treatments of wool. The possibility of using a water-soluble material which is compatible with usual anionic "detergents" (including soaps and synthetic surfactants), and which has no deleterious side effects, directly in the wash or dye bath so as to inhibit felting is a highly desirable adjunct to previous methods of shrinkage control, and offers the prospect to the consumer or finisher of being able to dye or launder finished garments, rather than having to depend on a questionable prior treatment of the yarn or fabric.

I have now found that felting shrinkage of animal hair fiber products and particularly wool yarn and yarn products may be controlled by wet processing wool in aqueous solutions which contain a water soluble condensation product having the probable structure:

(Structure I)



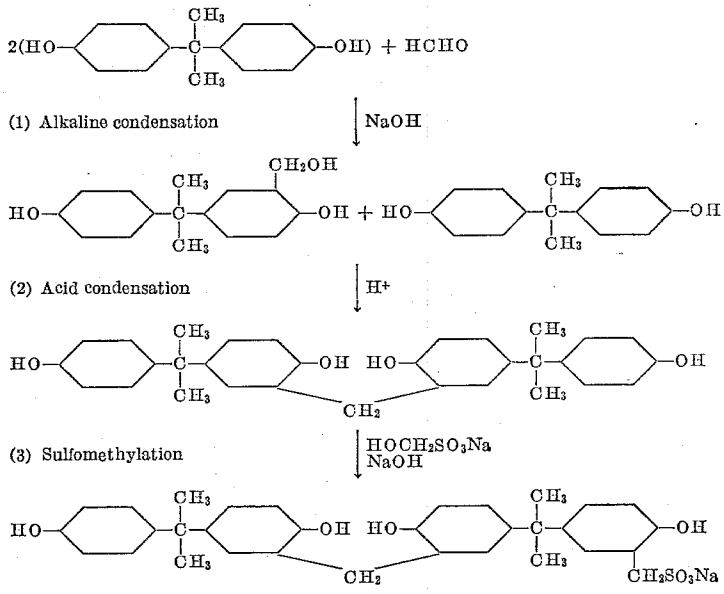
wherein R_1 represents the same or different low molecular weight alkyl groups (e.g., those having from one to four carbons), R_2 represents the same or different substituents selected from the group —H and —CH_3, m is an integer from 1 to 6, and X represents the substitution of an average of from 1 to 2 sulfomethyl groups for each four benzene nuclei in the total structure. Where alicyclic ketones such as cyclohexanone are employed in forming the precursors of these condensation products, the R_1 groups in the



portion will be linked.

Condensation products having this structure are prepared by a new process which involves condensing two moles of a bis-phenol (compounds produced by reacting a monohydric phenol which is unsubstituted in at least two of the ortho and para positions with an aliphatic or alicyclic ketone under acid conditions) with from about 1.0 to 1.8 moles of formaldehyde in alkaline solution, making the reaction mass strongly acid and heating to complete the condensation to a water insoluble resinous material, redissolving the resin by addition of alkali, and treating the solution with from about 1 to about 4 moles of formaldehyde-bisulfite adduct in order to introduce sufficient sulfomethyl groups to impart water solubility to the product.

The process used to produce the condensation products of this invention is thought to proceed by the following steps illustrated for a ratio of 2 moles of Bis-phenol A (the condensation product of two moles of phenol with one mole of acetone under acidic conditions) with one mole of formaldehyde:



An essential feature of this new process involves completely dissolving the bis-phenol compound in aqueous alkali (e.g., aqueous sodium hydroxide solution) before the addition of the formaldehyde. This assures uniformity of degree of polymerization of the final product by giving an even distribution of methylol groups in the available reactive ortho-phenolic positions. Upon acidification of the methylolated bis-phenol, methylene groups are formed between defferent bis-phenol molecules thereby producing condensation products of relatively low degree of polymerization, i.e., having from two to about seven bis-phenol units of structure in each chain. The number of bis-phenol units present will depend on the amounts of formaldehyde and bis-phenol units employed in the reaction mixture.

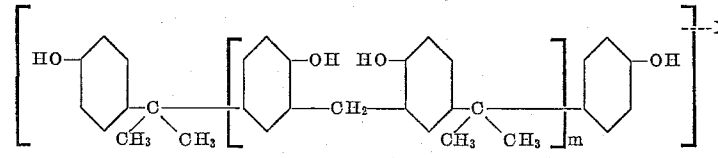
Where more than one mole of formaldehyde is employed in the alkaline condensation step, additional methylol groups will be introduced in the bis-phenol and thereby provide additional cross-linkable groups enabling condensation products of greater molecular weight to be formed.

The use of lower amounts of formaldehyde per bis-phenol unit (i.e., those nearer the 1:2 ratio) is preferred, since the polymeric water-insoluble resin formed in the alkaline and acid condensation is less viscous, more readily handled in manufacture, and is redissolved more easily before sulfomethylation. Desired anti-felting properties of the condensation products produced with the lower amounts of formaldehyde are equal to and in some cases superior to those of condensation products having a higher degree of polymerization.

Preferably, the product of the acid condensation should be completely redissolved before addition of the formaldehyde-bisulfite adduct—this assures uniformity and proper solubility of the final product, by providing even distribution of solubilizing sulfomethyl groups among and along the polymeric chains. Thus good solubility is achieved with a minimum number of sulfomethyl groups thereby assuring maximum effectiveness of the product.

It is preferred to employ sufficient formaldehyde-bisulfite adduct in the sulfomethylation step to assure reasonable solubility of the final product in cold water at customary laundering or dyeing liquor ratios. This level of sulfomethylation is achieved by use of from 1 to 4 moles of adduct for each two moles of original bis-phenol compound. In such cases, all of the adduct does not react, the amount entering into combination will depend on temperature and time of reaction as well as upon the amount of adduct initially present in the reaction mixture. Where the product of the acid condensation is polymerized to a degree that the polymer includes from 2 to 7 bis-phenol units, it is preferred to employ sufficient formaldehyde-bisulfite adduct to introduce an average of from 1 to 2 sulfomethyl groups for each four benzene nuclei in the polymer. Excessive sulfomethylation reduces the anti-felting action of the resins, presumably by lowering the substantivity of the products to wool.

Where 2 moles of Bis-phenol A are condensed as described above with 1 to 1.8 moles of formaldehyde and thereafter sulfomethylated, the resultant condensation products are believed to have the structure:



wherein *m* is an integer from 1 to 6, and X represents the substitution of an average of from 1 to 2 sulfomethyl groups for each four benzene nuclei in the total structure.

Suitable bis-phenols may be produced by acidic condensation of phenol or o-cresol with acetone, methyl ethyl ketone, cyclohexanone and similar low molecular weight ketones. Mixed bis-phenols prepared from phenol-cresol mixtures may also be used as well as mixtures of homogeneous bis-phenols.

The water-soluble resinous condensation products produced according to ths disclosure are, when isolated and dried, essentially colorless solids which have good thermal and light stability, i.e., do not yellow or otherwise discolor noticeably. They may be applied to wool and other animal hair fibers (cashmere, alpaca, mohair, etc.) from

aqueous baths at pH values of about 1 to about 9. They can be applied alone or in combination with aqueous solutions or baths containing anionic detergents, dyes, builders, buffers, salts, optical brighteners, etc. In such cases, it is preferred to employ concentrations which will give a pick up of the condensation product on the animal hair or wool of the order of 0.5 to 5% by weight.

The dried condensation products of this invention are compatible with anionic detergents and can be conveniently packaged and marketed as a mixture of the dry solids or as a concentrated aqueous solution of the detergent and the condensation product. Builders and buffer salts can also be incorporated in either the wet or dry mixes.

Although the condensation products of this invention can be applied at pH's ranging from about 1 to 9, best results are obtained where the application is made from a wash liquor or dye bath which is slightly on the acid side. Therefore, it is usually desirable to incorporate buffers which will compensate for differences in the pH of the water employed in the wet treatment, and also the acidity of the hair product undergoing treatment. Generally speaking, it is preferred to employ buffers which will give a pH to the treating liquor of from about 5 to 7.

The disclosed products have, in addition to anti-felting action, a marked beneficial effect in the removal of soil from wool fabrics. The mechanism of action of these products in increasing the detergency of certain anionic detergents, e.g., sodium dodecylbenzene sulfonate, is not known, but the effect is positive.

These two desirable properties of the condensation products of this invention make them of value generally in wet-processing operations such as scouring, bleaching, dyeing, stripping of dye, mothproofing, laundering, etc., on animal hair products and especially on wool.

The following examples will serve to illustrate the invention and in these examples, unless otherwise stated, the parts are expressed as parts by weight and temperatures are expressed on the centigrade scale:

EXAMPLE 1

Bis-phenol A (2,2-bis-(p-hydroxyphenyl)-propane) (456 parts, 2 moles) and 80 parts of sodium hydroxide are dissolved in 1000 parts of water at 60°, and 81 parts (1 mole) of 37% formaldehyde solution is added with continuous stirring. The temperature is raised to 90°, held there two hours, and then concentrated hydrochloric acid (265 parts) is added. The mixture separates into two phases, and with continued stirring, the mixture is heated for three hours at 95°. The pH is 1 to 1.5 during this time. The viscous organic layer is then redissolved completely by the cautious addition of sodium hydroxide (160 parts) as 50% solution. When solution is complete, a solution of formaldehyde-sodium bisulfite adduct (previously prepared from 162 parts (2 moles) of 37% formaldehyde solution, 165 parts of water, and 200 parts of sodium metabisulfite) is added, and the solution is stirred and heated for 18 hours at 95° C. After cooling, the pH of the resultant clear solution is adjusted to 6.0 by addition of 420 parts of concentrated hydrochloric acid, 200 parts of sodium chloride is added, and the precipitated solid is filtered and dried, giving 710 parts of colorless solid which is readily soluble in cold water to yield a clear solution.

Table I, which follows, lists Examples 2 to 21 wherein are shown additional representative methods of proceeding to yield products of the disclosed type, all having properties which make them useful for the purposes previously described in this disclosure. Additional variations in ratios of reactants will be obvious to those skilled in the art, and these examples are intended to be only representative rather than all-inclusive.

Table I

Ex. No.	Bis-phenol A used (moles)	Formaldehyde used (moles)	NaOH used for resolution (parts)	Formaldehyde-bisulfite adduct used (moles)
2	0.5	0.25	30	0.25
3	0.5	0.25	30	0.30
4	0.5	0.25	35	0.35
5	0.5	0.25	40	0.40
6	0.5	0.25	40	0.50
7	0.5	0.25	40	0.60
8	0.5	0.25	40	0.70
9	0.5	0.25	40	0.80
10	0.5	0.265	40	0.50
11	0.5	0.284	40	0.50
12	0.5	0.309	40	0.50
13	0.5	0.333	28	0.25
14	0.5	0.333	32.5	0.30
15	0.5	0.333	37.5	0.40
16	0.5	0.333	40	0.50
17	0.5	0.40	40	0.30
18	0.5	0.40	40	0.50
19	0.5	0.40	40	0.80
20	0.5	0.415	40	0.50
21	0.5	0.415	40	0.75

In each of the above examples (2 to 21 inclusive) the procedure of Example 1 is followed, in each case employing 250 parts of water and 20 parts of sodium hydroxide for the initial solution. After methylolation 65 parts of concentrated aq. hydrochloric acid is added and the mixture heated as in Example 1. The NaOH used for redissolving the polymer is added as 50% solution, and following completion of solution of the polymer, the $HOCH_2—SO_3Na$ is added as solution in water. The final solution, after heating 18 hours or longer, is cooled, neutralized, salted, if desired to precipitate the product before drying, and dried conventionally or spray dried.

EXAMPLE 22

2,2 - bis - (4 - hydroxy - 3 - methylphenyl) - propane (102.4 parts, 0.4 mole) (prepared by condensation of o-cresol with acetone under acidic conditions) is dissolved at 70° in 250 parts of water containing 32 parts of sodium hydroxide. To this solution is added with continuous stirring 16.2 parts of 37% formaldehyde solution, and the temperature is held at 80° for three hours. Then 125 parts of concentrated aqueous hydrochloric acid is added and the temperature held at 95° for two hours. The viscous precipitated resin is then redissolved by addition of 40 parts of sodium hydroxide as 50% solution. After all is in solution, a solution of 0.4 mole of formaldehyde-bisulfite adduct (prepared from 32.4 parts of 37% formaldehyde solution, 40 parts of water and 40 parts of sodium metabisulfite) is added. Following an 18 hour period of heating and stirring at 95°, the resultant solution is cooled, adjusted to pH 6 with hydrochloric acid, salted with 30 parts of sodium chloride, filtered and dried giving 157 parts of a colorless water-soluble powder.

EXAMPLE 23

A laundering bath is prepared by dissolving 4 parts of the product of Example 1 and 2 parts of sodium dodecylbenzene sulfonate in 2000 parts of water at 120° F. A second laundering bath is prepared by dissolving only 2 parts of sodium dodecylbenzene sulfonate in 2000 parts of water at 120° F.

Into these baths in tumble type washers are entered identical knitted wool garments previously equally soiled (with a synthetic soil of a standard type) and weighing 100 parts each. The garments are washed in conventional fashion for 15 minutes, rinsed, spun dry and dried. The garment washed in the bath containing the product of Example 1 is free of soil and nearly free of felting shrinkage. The garment washed in the bath containing only anionic detergent is still soiled and shows signs of felting.

The washing cycles are repeated using fresh baths for each cycle. After six cycles, the garment washed in deter-

gent only is badly felted and no longer usable, while the treated garment is still in good condition.

EXAMPLE 24

1, 1-bis-(4-hydroxyphenyl)-cyclohexane (80.4 parts, 0.3 mole) (prepared by acid condensation of cyclohexanone with phenol) is dissolved at 90° in 200 parts of water containing 24 parts of sodium hydroxide. To this solution is added with continuous stirring 12.2 parts of 37% formaldehyde solution, and the temperature is maintained at 90° for three hours. Then 75 parts of concentrated hydrochloric acid is added and the temperature is kept at 90° for three hours.

A 50% aqueous solution of 40 parts of sodium hydroxide is added, and the mixture is heated and stirred until the precipitate has dissolved. A solution of 30 parts of sodium bisulfite and 24.3 parts of 37% formaldehyde in 30 parts of water is added. The reaction mixture is heated for 18 hours at 90°, with constant agitation. The product is precipitated by adjusting the pH to 6, separated, and dried, giving 123 parts of colorless solid having anti-felting properties when applied to wool in similar manner to that described in Example 23.

EXAMPLE 25

(A) *Dyeing using the product of Example 1.*—A loosely knit wool fabric weighing 380 parts is placed in a dyebath prepared from 2.28 parts of C.I. Acid Yellow 40, 0.76 part of C.I. Acid Red 114, 0.76 part of C.I. Acid Blue 78, 15.2 parts of the product of Example 1, 7.6 parts of acetic acid and 9500 parts of water. The fabric is agitated for one hour at 180° F. in the dyebath to effect exhaustion of the dye from the bath and give a level dyeing on the fabric. It is then rinsed, spun-dry, and dried in a forced-draft air drier at 170° F. The fabric shows no evidence of felting and is dyed a uniform brown shade.

(B) *Control dyeing.*—An identical loosely knit wool fabric to that dyed in A weighing 380 parts is placed in a dyebath prepared from 2.28 parts of C.I. Acid Yellow 40, 0.76 part of C.I. Acid Red 114, 0.76 part of C.I. Acid Blue 78, 7.6 parts of acetic acid and 9500 parts of water. The fabric is dyed, rinsed and dried under the identical conditions employed in A. The brown dyed fabric is

badly felted, evidenced by matting of the wool fibers and a large reduction in area of the fabric.

EXAMPLE 26

In Example 1, while otherwise proceeding as described, if the 456 parts of the bis-phenol A is replaced with 484 parts of 2,2-bis(p-hydroxy phenyl)-butane, a water soluble colorless solid is obtained having properties similar to those of the product of Example 1.

I claim:

A process for preparing a water soluble condensation product which comprises dissolving 2,2-bis(4-hydroxyphenyl) propane in aqueous alkali, condensing 2 moles of the solubilized alkaline bis-phenol with from 1 to 1.8 moles of formaldehyde at temperatures up to reflux, strongly acidifying the reaction mass and heating the acidified mixture to temperatures up to reflux to complete the condensation to a water insoluble resinous material, redissolving the resinous material in aqueous alkali, reacting the redissolved resin in the presence of a compound consisting of from about 1 to 4 moles of formaldehyde-bisulfite adduct at temperatures up to reflux to introduce an average of from 1 to 2 sulfomethyl groups for each four benzene nuclei in the total structure, precipitating the water soluble condensation product by acidifying and salting the reaction mass and then recovering the precipitated condensation product.

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