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FIXATION OF SIZES

Louis H. Bock, Glenside, and Alva L. Houk, Philadelphia, Pa., assignors to Röhm & Haas Company, Philadelphia, Pa.

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This invention relates to an improved process for converting water-soluble or water-dispersible, high molecular weight compounds containing a multiplicity of hydroxyl groups into complexes which are insoluble in water. It deals with the insolubilization of polymeric hydroxyl-containing products, such as polyvinyl alcohol and the polyoses which include water-soluble, amylaceous and cellulosic sizing materials, by reaction of these materials with aminomethylene amino-1,3,5-triazines. More particularly this invention relates to improving the "fastness" of films or coatings of polyhydroxy, water-soluble sizing materials, and finishing materials alone or upon textile fabrics, yarns, fibers and similar materials by the use of condensation products obtainable from amino-1,3,5-triazines, formaldehyde, and non-aromatic amines having at least one hydrogen atom attached to the nitrogen.

While the high molecular weight, hydroxyl-containing substances, which are readily dispersed in water, are applied economically and efficiently to fabrics, they are for the same reason easily removed again by water. For example, starch, the most common type of coating or sizing material, is removed by laundering. Efforts to improve the fastness or resistance of sizes to washing have primarily been concerned with the substitution of special sizing materials for the more common, economical sizes and have required special solvents or unusual steps in processing. In another type of procedure resin-forming compounds have been used to impart fastness to size on fabrics by formation of protective, adhering films, whereas in the present invention compounds are employed which actually combine with polyhydroxy sizing materials under conditions requiring no harmful or severe treatment of the size or fabric and no processing steps which are foreign to standard textile mill practice.

An object of this invention is to provide a more suitable method than has heretofore been available for rendering any water-soluble, hydroxyl-containing, sizing material insoluble. It is a particular object to render insoluble such sizing materials as starch, in its various forms, polyvinyl alcohol, and water-dispersible cellulosic derivatives. It is also an object to stiffen fabrics permanently. It is a further object to provide an improved one-bath process for the fixation of water-dispersible, hydroxyl-containing sizing materials on textile fabrics, yarns, fibers, straw, paper and similar materials.

These objects are accomplished by treating and heating a water-soluble size with a condensate of

an amino-1,3,5-triazine with formaldehyde and a strongly basic, non-aromatic monoamine having at least one hydrogen on the nitrogen. The preparation of such condensates is described in our copending application Serial No. 300,548, filed October 21, 1939, which, on August 6, 1940, issued as U. S. Patent 2,210,831. The preferred condensates are those prepared from primary or secondary amines having substituents of less than nine carbon atoms. The use of the general type of compounds of which the aminomethylene amino-1,3,5-triazines represent a preferred species, for the purpose of improving the fastness of water-dispersible sizes has been described in our co-pending application Serial No. 267,342, filed April 11, 1939, which, on November 5, 1940, issued as U. S. Patent 2,220,508, and the present application represents a continuation-in-part thereof.

The aminomethyleneamino-1,3,5-triazines may be made according to the methods indicated in co-pending application Serial No. 300,548 (now U. S. Patent 2,210,831). Several examples are given therein for the preparation of such compounds. It appears that the formaldehyde serves as a link between the triazine and the monoamine, as the names of the resultant products would indicate. It appears that, in effect, the oxygen atom of the formaldehyde combines with a hydrogen atom from the amino group of the amino-1,3,5-triazine and with a hydrogen atom of the amino group of the non-aromatic monoamine, thereby linking the two together through the methylene group.

The condensates of amino-1,3,5-triazines, formaldehyde, and the non-aromatic monoamines combine at moderately elevated temperatures with polyhydroxy sizing materials to yield relatively insoluble complexes or reaction products. The preferred sizing materials which are contemplated in this invention are the water-soluble cellulose ethers, such as water-soluble methyl or ethyl cellulose and hydroxyethyl cellulose, polyvinyl alcohol and starch, such as corn, rice, tapioca, sago, wheat or potato starch, flours containing a high percentage of starch, and the many modified and treated forms of starch which are used for sizing, including acid or enzyme converted starch pastes, oxidized starch, the hydroxyl-containing derivatives of starch, such as ethyl starch, and the products of hydrolysis including dextrines and sugars. These materials are all here classified as water-soluble sizing materials, since they yield either true solutions or

colloidal solutions or dispersions which allow their ready removal as in laundering.

The aminomethylene aminotriazines have been found to react with polyhydroxy sizing compounds at mildly elevated temperatures, with or without the presence of alkaline or acidic catalysts, such as sodium carbonate or bicarbonate, sodium acetate, one of the ammonium phosphates, ammonium chloride, acetic acid, etc. It will be observed that such catalysts are for the most part buffer salts of a weak acid and strong base or of a strong acid and a weak base.

In the preferred procedure for the application of polyhydroxy sizing materials to textile fabrics, yarns, and the like, a sizing bath is prepared and to this bath is added an aminomethylene aminotriazine. Suitable compositions for sizing contain about two parts of such a compound to about one to ten parts of size. The size-fixing compound may be added directly to the bath and dissolved or dispersed therein or it may be added to the bath in the form of an amine salt of an organic or inorganic acid. The acids seem to have a catalytic effect. There may also be used the quaternary salts of these amines. The sizing bath is used to impregnate or coat fabric, yarn, etc. by any of the usual sizing methods, such as dipping or spreading, followed by squeezing with rolls or scraping with a doctor blade. The treated fabric or yarn may then be dried, if desired, or it may pass directly to an apparatus in which it is dried and heated above 90° C.

The aminomethylene amino-1,3,5-triazines have the advantage over other compounds which at least theoretically should react with hydroxyl groups, in that they react with starch and other polyhydroxy sizing materials at relatively low temperatures and in a short period of time. While in general temperatures between 100° C. and 120° C. are most desirable for insolubilizing size according to this process, the effect is noticeable at 80° C. and, of course, is obtained at temperatures above 120° C. even more rapidly than in the preferred range. At elevated temperatures, however, some starch derivatives tend to yellow and for this reason such temperatures should be avoided, especially on white fabrics. Heating may be accomplished while fabric or yarn is passed over heated rolls or through a hot oven, such as a closed tenter, loop drier, or the like.

An advantage of these fixation agents is that they permit a one-bath sizing operation. Yet these compounds are also effective when applied to fibers, yarns, fabrics, or non-fibrous or fibrous sheets subsequent to the application of hydroxyl-containing sizing material. Mixtures containing both size and fixing agent may be prepared ready for use. Similar compositions may be prepared in which the size is partially toughened or pretreated before application as a sizing material. Such compositions are of interest in particular in the treatment of fibers as in making paper. But following any variation in the sizing procedure, it is necessary in a late step to heat to secure the highest degree of fixation of the size. The sized material may then be washed, if desired, to remove by-products, unreacted material, etc.

The process of insolubilizing hydroxyl-containing, water-soluble sizes and improving their wash-fastness on fabric, as herein described, may be applied to yarn, fabric, thread, fibers or sheets of any material which may be wet-treated and heated to 90° C. without undue damage. The

process is of particular interest in the sizing of such materials as cotton, linen, paper, straw, jute, hemp, and the various synthetic fibers and non-fibrous sheets.

The condensates of amino-1,3,5-triazines with formaldehyde and a strongly basic, non-aromatic, non-tertiary amine, referred to as aminomethylene amino-1,3,5-triazines, are obtained by heating together the three reactants with or without solvent. There may be condensed with any amino-1,3,5-triazine at least one mol each of aldehyde and amine, and more in many cases. For example, melamine may react with as many as three mols of each, diacylammelines also with as many as three mols of each. Typical compounds may be obtained from ammelide, ammeline, melamine, thioammelne, and their derivatives which still possess at least one amino group. Of particular interest are the substituted triazines such as the diacyl ammelines, the preparation of which is described in our copending application Serial No. 300,549, filed October 21, 1939, which, on February 17, 1942, issued as U. S. Patent 2,273,687, by means of which long-chained groups may be imparted to polyhydroxy, sizing materials. Other typical triazines are 2-chloro-4,6-diamino-1,3,5-triazine and 1-cyano-2-amino-4,6-dimethyl-1,3,5-triazine.

Details of the sizing of fabrics will be evident from the following examples:

Example 1

Cotton fabric was coated with an aqueous paste containing 4% of water-soluble ethyl cellulose, 0.48% of bis (dimethylaminomethyl) thioammelne and 0.5% of sodium carbonate. The excess was squeezed off, the material was dried at room temperature, and was then heated one-half hour at 130° C. It was washed thoroughly and ironed. A very stiff finish resulted, permanent to washing.

Example 2

Cotton fabric was coated with an aqueous solution containing 6.5% of water-soluble hydroxyethyl cellulose, and 2.2% of tris (dimethylaminomethyl) melamine in the form of the hydrochloride. It was treated as in Example 1. The finish was very stiff and not affected appreciably by further washing.

Example 3

Viscose rayon fabric was coated with a paste containing 5 parts of an 8% potato starch paste and 1 part of the dimethylaminomethyl derivative of 1-cyano-6-imino-2,4-dimethyl-hexahydro-1,3,5-triazine as the acetate. Treated as in Example 1, the fabric obtained a stiff finish, resistant to further washing.

Example 4

A cellulose acetate fabric was coated with a composition comprising 3 parts of 8% potato starch paste and 1 part of 25% solution of bis-dimethylaminomethyl diacetyl ammeline, acetic acid salt. Treated as in Example 1, a stiff, wash-resistant finish resulted.

Example 5

Linen cloth was coated with an aqueous solution containing 5.85% of hydroxyethyl cellulose and 4.17% of bis-dimethylaminomethyl thioammelne hydrochloride. It was treated as in Example 1. A very stiff, permanent finish was produced.

Example 6

Cotton sheeting was coated with a composition prepared from 5 parts of an 8% tapioca starch paste and 1 part of bismorpholinomethyl ammelide hydrochloride. When the sheeting had been dried and heated as in Example 1, a smooth, stiff finish resulted, fast to washing.

Example 7

To 20 parts of a 4.2% aqueous solution of water-soluble ethyl cellulose and 1 part of bis (dimethylaminomethyl) ammelide was added 0.5% of sodium carbonate, and the mixture diluted with 25% of its weight of water. It was spread out on a glass plate in the form of a film, dried, and heated 30 minutes at 130° C. The film was removed and soaked in water. It did not dissolve.

Example 8

A mixture of 20 parts of a 7.5% aqueous solution of water-soluble hydroxyethyl cellulose and 1 part of tris (dimethylaminomethyl) melamine was made just acid with HCl, and further diluted with about one-fourth its volume of water. It was spread out in a film and treated as in Example 1. The film became insoluble in water.

Example 9

Example 2 was repeated using an 8% potato starch paste instead of the hydroxyethyl cellulose. The starch film did not swell in boiling water.

We claim:

1. A process for insolubilizing water-soluble, hydroxyl-containing sizing material which comprises treating said material with a condensation product of an amino-1,3,5-triazine and at least one mol each of formaldehyde and a strongly basic, non-aromatic amine having less than nine carbon atoms in any single group attached to the nitrogen and having at least one reactive hydrogen attached to the nitrogen atom, and heating said treated material.
2. A process for insolubilizing water-soluble, hydroxyl-containing, sizing material which com-

prises treating said material with the condensation product of an amino-1,3,5-triazine, formaldehyde, and a strongly basic, non-aromatic, secondary monoamine, having less than nine carbon atoms in each nitrogen substituent, and heating said treated material.

3. A process for improving the wash fastness of water-soluble, hydroxyl-containing size, which comprises treating textile material with said size and with a condensation product of an amino-1,3,5-triazine and at least one mol each of formaldehyde and a strongly basic, non-aromatic amine having less than nine carbon atoms in any single group attached to the nitrogen and having at least one reactive hydrogen attached to the nitrogen atom, and heating said treated textile material.

4. A process for improving the wash-fastness of water-soluble, hydroxyl-containing size, which comprises treating textile material with said size and with a condensation product of an amino-1,3,5-triazine, formaldehyde, and a strongly basic, non-aromatic secondary monoamine having less than nine carbon atoms in each nitrogen substituent, and subsequently heating the treated textile material.

5. The process of claim 4 in which the water-soluble, hydroxyl-containing size is a starch sizing.

6. The process of claim 4 in which the water-soluble, hydroxyl-containing size is a cellulose ether sizing.

7. The process of claim 4 in which the water-soluble, hydroxyl-containing size is a polyvinyl alcohol sizing.

8. The process for improving the wash-fastness of a water-soluble, hydroxyl-containing size which comprises treating textile material with said size and with the condensation product of melamine and at least one molecular proportion each of formaldehyde and dimethylamine, and subsequently heating the treated textile material.

LOUIS H. BOCK.
ALVA L. HOUK.