Patented Aug. 7, 1945 2,381,752

UNITED STATES PATENT OFFICE

2,381,752

PROCESS OF INSOLUBILIZING PROTEIN AND PRODUCT

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No Drawing. Application December 31, 1943, Serial No. 516,586

16 Claims. (Cl. 106—125)

This invention relates to insolubilizing water-soluble proteins and rendering them hydrophobic, is more particularly directed to processes and compositions in which a soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms are dissolved in a mutual solvent and, preferably the solution is heated, whereby a water-soluble complex compound of the protein and chromium compound is formed, and is further directed to processes in which solvent is removed from such compositions and to the insoluble, hydrophobic chromic-protein products thus obtained.

Proteinaceous materials have been widely used as coating compositions, sizes, textile finishes, and for other similar purposes. For instance, animal glue or gelatin has been employed for coating and filling paper. Various hardening and insolubilizing agents have been used with the glue to make it less readily leachable with water. However, with the hardening and insolubilizing agents heretofore available, the glue or similar proteinaceous material has retained its original tendency to be softened or dispersed in water even though not actually dissolved; in other words, the coating has tended to be hydrophilic. This hydrophilic character of such coatings has been objectionable and has prevented their use in many applications where they would otherwise have been satisfactory.

In my United States Patent 2,273,040, issued February 17, 1942, Serial No. 358,479, and my application Serial No. 402,995, filed July 18, 1941, I have described certain water-soluble complex compounds of the Werner type in which trivalent nuclear chromium atoms are coordinated with carboxylic acido groups having at least ten carbon atoms and the application of such compositions to the surfaces of various materials to increase the hydrophobic character of the surfaces. While the surfaces of proteinaceous bodies, such as glue coatings, may thus be made water-repellent, there are many situations in which a surface type of coating, no matter how effective, is not adequate. For instance, when bodies or articles coated with glue are subject to wear and abrasion, any treatment which makes only the surface hydrophobic will soon be worn off and its effectiveness will be lost. In such cases it is important to impart to the coating a substantially uniform hydrophobic character throughout a substantial thickness. The problem thus becomes one of providing a method for improving the glue or other proteinaceous material so as to make it insoluble and hydrophobic instead of soluble and hydrophilic.

Now I have found that proteins which ordinarily are water-soluble and hydrophilic may be insolubilized and rendered hydrophobic by dissolving in a mutual solvent such a protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms, such as described in my aforementioned patent applications, Serial Nos. 358,479 and 402,995, and preferably heating this solution, whereby a novel water-soluble complex compound of the protein and Werner compound is formed, and by removing solvent from such solutions, whereby insoluble, hydrophobic, chromic-protein products are obtained.

The field of usefulness of proteins is extended through the application of my invention. By incorporating a relatively small proportion of the complex chromium compound into glue, for instance, and coating or impregnating paper with the resultant composition, a coated or filled paper is obtained which is highly resistant to both oil and water. In contrast, paper coated with glue by methods heretofore available, while resistant to oil, is hydrophilic and readily softened by water. Moreover, the water-resistant coatings of my invention have substantial thickness and can stand considerable handling and abrasion without being rubbed off.

In describing my invention, it is necessary to use certain terms pertaining to the behavior of substances with respect to water, and while these terms are used in their accepted and ordinary meaning, the nature of my invention may perhaps be made more clear by a fuller understanding of such terms. Thus, by "soluble" is meant the property of mixing with a liquid to form a homogeneous mixture, while "insoluble" means a lack of such property. "Hydrophilic" refers to the ability of a substance to absorb or adsorb water, and conversely, "hydrophobic" refers to a lack of such ability. In other words, a substance may be insoluble in water but nevertheless hydrophilic, that is, it may not dissolve in the water to make a homogeneous mixture, but at the same time it may absorb water, swelling up and becoming slimy or sticky. On the other hand, hydrophobic substances are substantially impervious to the action of water and tend to be water-repellent, that is, to resist wetting by water.

The present invention comprehends the treatment of any soluble protein. The protein may be of either animal or vegetable origin, and may be simple, conjugated, or derived. Representative of the soluble proteins are, for instance, albumens, histones, protamines, and peptones. Gelatin, and its impure form, glue, may be employed to especial advantage.

The chromium compound used with a soluble protein, according to my invention, should be a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms. Such compounds may be prepared by processes in which contact, in the substantial absence of free water, is effected between carboxylic acido groups having at least ten carbon atoms and basic trivalent chromium salts having a basicity no greater than about 50%. Such preparations, employing acyclic acido groups are described fully in my U. S. Patent 2,273,040. Processes using cyclic acido groups, such as abietic, naphthenic, or naphthoic acid groups, are carried out as described in my previously-mentioned patent application, Serial No. 402,995, filed July 18, 1941, that is, by effecting contact, in the substantial absence of free water, of a carbocyclic carboxylic acido group having at least ten carbon atoms with a basic trivalent chromium salt of a monobasic acid, the basicity of the chromium salt being no greater than about 50%. The basic trivalent chromium salt may be one such as described in the abovementioned Patent 2,273,040 and contact may be effected as also described therein. Likewise, the terms "free water," "acido groups" and "functional acido group" are used herein in the sense defined in that patent.

If the functional acido groups are carbocyclic, they must contain more than ten carbon atoms and these carbon atoms must be present in a cyclic structure, but the cyclic structure may comprise a single ring or a number of rings and a portion of the carbon atoms may be present as the side chains. The acidic nature of the group must be due to a carboxyl group, but this may be present either on the cyclic structure directly or on a side chain. Typical, therefore, of the cyclic carboxylic acido groups which may be employed are aryl carboxylic acids such as those having a benzene ring nucleus with carbon chain substitutions on the ring, alpha- and beta-naphthoic acids, and those having more complicated ring structures such as those derived from phenanthrene. The abietic acid in rosin, being methyldecahydroretene carboxylic acid, may be regarded as being of the latter type. The cyclic group may be a saturated ring such as occurs in cyclodecane and its homologues. The ring structure may be aralkyl, containing an aryl group as a substitution on an alkyl group to which the carboxyl group is attached as in the case of naphthyl-acetic or -propionic acids. It will be seen, therefore, that the functional acido groups may have any configuration so long as there is present a ring structure and the entire group contains at least ten carbon atoms.

For convenience of reference chromium coordination compounds as above described will hereinafter be referred to as "Werner complexes."

While any of the Werner complexes referred to in my beforementioned patent applications may be employed in the present invention, I prefer to use, of the acyclic compounds, stearato chromic chloride, palmitato chromic chloride, or laurato chromic chloride, and of the carbocyclic compositions, abietato chromic chloride, naphthenato chromic chloride, or naphthoato chromic chloride.

The proportion of Werner complex required for treatment of a soluble protein, according to my invention, may be considerably varied. The proportion should be at least large enough to exhibit a definite effect, but on the other hand, the proportion required to show an effect is usually surprisingly small. I have found that if the weight of soluble protein is about from 10 to 200 times the weight of Werner complex a marked effect is obtained, and for best results, particularly with glue, I prefer to use a weight of glue about from 20 to 100 times the weight of the Werner complex, the preferred complex for these proportions being stearato chromic chloride.

Having selected a soluble protein and a Werner complex in the desired proportions, these components are then dissolved in a mutual solvent. The components may be dissolved in separate portions of solvent and the solutions obtained may be mixed, or they may be dissolved simultaneously or consecutively in the same body of solvent. The solvent should be one capable of holding both the protein and Werner complex in solution. Water may be employed as the mutual solvent, although in some circumstances it may be preferred to dissolve the protein in water and the Werner complex in an organic solvent, such as ethanol or isopropanol, which is compatible with water. Obviously, the ultimate mutual solvent will in such a case be a mixture of alcohol and water.

The concentration of protein-Werner complex mixture in the solution thus obtained may be widely varied. If the solution is to be stored or shipped, it will, for economic reasons, be desirable to have a relatively large proportion of solid ingredients in the solution, but on the other hand, if the solution is made up at its point of use a dilute solution may be equally advantageous. Ordinarily, it is preferred that the solution contain about from 2 to 50% of solids.

The protein and Werner complex appear to be present in the mutual solvent in the form of some kind of complex. This complex forms spontaneously in the solution upon standing and its formation may be accelerated by heating the solution. It is definitely undesirable, however, to continue the heating for too long a time, since this tends to make the solution unstable. Best results are obtained by heating the solution nearly to the boiling point momentarily and then cooling.

From the novel solutions of my invention, obtained as above described, water-insoluble hydrophobic products may be obtained by removal of the solvent. Such removal may be accomplished by techniques with which the art is already familiar, such as evaporating at elevated temperature and if desired under reduced pressure. The form in which the final product is desired will in many instances determine the manner of solvent removal. Thus, for coating paper, the solution may be run upon the paper and dried as a coating on the paper, optionally under calendering rolls. On the other hand, if a cast film is desired the solution may be run upon a heated casting surface and dried as a sheet.

The precaution above noted against prolonged heating of the protein-Werner complex solution

obviously does not apply when insolubilization of the product is desired, but on the contrary, it may be desirable to heat the dried product at an elevated temperature for a period long enough to insure complete solvent removal, since by such drying, if the solvent be water, an irreversible dehydration takes place.

The product obtained is characterized by being hydrophobic and insoluble in water. It may be in the form of a film, a fiber, a solid body, or a coating or impregnation upon a supporting body such as paper or textile.

The processes and compositions of the present invention may find use in a wide variety of applications. Thus, the solutions may be used as coating compositions, adhesives, water paints, and plastics and in the production of synthetic fibers. In all of these applications insolubilization of the protein is often desired, and the methods of this invention are very useful in effecting such insolubilization. Water-impervious films may likewise be produced according to this invention.

The nature of my invention will be better understood by reference to the following illustrative examples, but these examples are to be construed only as expositive and not as limiting.

Example 1 illustrates the practice of the invention where the soluble protein is glue and the Werner complex is stearato chromic chloride.

Example 1

A solution of this invention was made by dissolving 25 grams of hide glue and 8 grams of glycerin in water to give a total volume of 200 cc. To 100 cc. of this solution was added 0.92 cc. of a 33% solution of stearato chromic chloride in alcohol. There was thus obtained a solution which showed no sign of precipitation after standing for 12 hours. This solution was used for treating paper by dipping the paper in the solution and drying. The treated paper was very resistant to water and oil, and the glue coating was isoluble and hydrophobic in that it did not dissolve or become slimy when soaked for several hours in water.

An even more hydrophobic film was prepared by using 2.6 cc. of 33% solution of stearato chromic chloride in alcohol to 100 cc. of glue solution as above described.

A composition particularly useful for coating paper and textiles is produced by adding paraffin wax to a protein-Werner complex composition, as described in Example 1. In such a composition the Werner complex appears to act as a dispersing agent for the paraffin wax. This is illustrated in Example 2.

Example 2

In 200 parts by weight of water there was dissolved 10 parts of animal glue and to the homogeneous solution obtained there was added 6 parts of 33% solution of stearato chromic chloride in alcohol with intense agitation. The mixture was warmed to a temperature 15° C. higher than the melting point of paraffin wax and there was then added 100 parts of molten paraffin wax with violent agitation. By this procedure the wax was well emulsified. The pH of the mixture was then raised to 7.0 by the addition of aqueous ammonia. The resulting mixture was a thin, uniform, white fluid showing no tendency to settle or cream. One part of this emulsion was added to 9 parts of water to obtain a dilute wax emulsion which was then applied to paper and fabric by dipping the paper and fabric in the solution and drying at 100° C. for five minutes. The coated paper and fabric thus obtained were highly water-repellent.

While in the foregoing description of my invention I have shown certain specific compositions and processes, it will be understood that without departing from the spirit of my invention one skilled in the art may employ numerous processes and produce various compositions.

I claim:

1. In a process for producing soluble complex compounds of protein and chromium, the step comprising dissolving a water-soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms in a mutual solvent.

2. In a process for producing soluble complex compounds of protein and chromium, the steps comprising dissolving a water-soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms in a mutual solvent and heating the solution.

3. In a process for producing soluble complex compounds of protein and chromium, the step comprising dissolving stearato chromic chloride and glue in water.

4. In a process for producing soluble complex compounds of protein and chromium, the steps comprising dissolving stearato chromic chloride and glue in water, the weight of glue being about from 20 to 100 times the weight of stearato chromic chloride, and heating the solution.

5. A composition comprising a solution of a water-soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms in a mutual solvent.

6. A composition comprising an aqueous solution of a water-soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms in a mutual solvent.

7. A composition comprising an aqueous solution of stearato chromic chloride and glue.

8. A composition comprising an aqueous solution of stearato chromic chloride and glue, the weight of glue being about from 20 to 100 times the weight of stearato chromic chloride.

9. A composition comprising an aqueous solution of stearato chromic chloride and glue, having paraffin wax emulsified therein, the weight of glue being about from 20 to 100 times the weight of stearato chromic chloride.

10. In a process for producing insoluble, hydrophobic chromic-protein products, the steps comprising dissolving a water-soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with a carboxylic acido group having at least ten carbon atoms in a mutual solvent and thereafter removing the solvent from the solution.

11. In a process for producing insoluble, hydrophobic chromic-protein products, the steps comprising dissolving stearato chromic chloride and glue in water, and evaporating the solution substantially to dryness.

12. In a process for producing insoluble, hydrophobic chromic-protein products, the steps

comprising dissolving stearato chromic chloride and glue in water, the weight of glue being about from 20 to 100 times the weight of stearato chromic chloride, heating, and evaporating the solution substantially to dryness.

13. An insoluble, hydrophobic chromic protein composition comprising the reaction product obtained by dissolving a water-soluble protein and a water-soluble complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with carboxylic acido group having at least ten carbon atoms in a mutual solvent, heating, and evaporating the solution substantially to dryness.

14. An insoluble, hydrophobic chromic-protein composition comprising the reaction product obtained by dissolving stearato chromic chloride and glue in water, heating, and evaporating the solution substantially to dryness.

15. An insoluble, hydrophobic chromic-protein composition comprising the reaction product obtained by dissolving stearato chromic chloride and glue in water, the weight of glue being about from 20 to 100 times the weight of stearato chromic chloride, heating, and evaporating the solution substantially to dryness.

16. An insoluble, hydrophobic chromic-protein composition comprising the reaction product obtained by dissolving stearato chromic chloride and glue in water, the weight of glue being about 20 to 100 times the weight of stearato chromic chloride, and emulsifying paraffin wax therein, heating, and evaporating the emulsion substantially to dryness.

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