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MANUFACTURE OF CONDENSATION PRODUCTS

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This invention relates to the manufacture of condensation products, and its primary objects include the provision of efficient and inexpensive tanning agents and simplified economical procedure for making such agents; further objects being to afford improved methods of manufacturing water-soluble condensation products comprising sulfones or the like, without complicated or costly steps heretofore employed, and to provide new and particularly satisfactory products of such character. Other objects and advantages include those which are hereinafter set forth or are incidental to the novel procedure and products hereinafter described.

It has been known that certain sulfones have useful properties as tanning agents, but their manufacture for such purpose has in general been complicated and has involved difficulty in achieving a product that at the same time has good tanning characteristics, is suitably colorless and is properly soluble in an acid medium of the sort used in tanning. Thus, procedures heretofore available for making such products have involved a variety of special or difficult treatments, e. g., the use of successive condensation steps, careful control to isolate or purify particular intermediate or end products, the use of pressure apparatus for condensation of specific sulfones, and special alkaline treatments of sulfonic acid compounds. I have discovered, however, that a remarkably satisfactory condensation product, having excellent qualities as a tanning agent, may be produced by a simplified and inexpensive process involving, for example, the following steps: An oxybenzene derivative, such as phenol, cresol or xylenol, or a mixture of two or more such substances, is subjected to a relatively simple sulfonation, preferably in the presence of a high percentage of sulfuric anhydride (e. g., SO_3). The resulting product, without preliminary or other alkaline treatment and without any special preliminary condensation step, is then subjected to condensation in the presence of a suitable aldehyde compound and a salt of sulfurous acid, preferably at boiling temperature and at atmospheric pressure; and the resulting product of condensation may thereafter, as I have found, be readily decolorized by treatment with a simple bleaching agent, and may be readily adjusted to a good tanning pH with mineral or organic acids or acid salts. The product so treated, is found to be an excellent tanning agent which does not stain or discolor the leather and which may be used to produce a well filled white leather satisfactorily fast to light.

In practice, it has been found particularly desirable to carry out the sulfonation step at a relatively high temperature, e. g., 160° to 180° C., and at atmospheric pressure; the preferred sulfuric agent being oleum, preferably so-called 65% oleum (i. e., containing approximately 65% SO_3 and 35% H_2SO_4), which represents the highest content of SO_3 commercially available in oleum at present. Upon the basis of tests which are deemed to be reliably indicative, the product of the sulfonation is believed to consist of a mixture of the original oxybenzene derivative in a free state, in a sulfonic acid state, and in a sulfone state. For best results, it is likewise believed that the sulfone content should be as high as possible, and that the production of a high sulfone content is at least an important reason for the excellent results which are in fact obtained when the SO_3 content of the oleum used is of the order of 65%. In some cases, good results may be had with oleum containing as low as 50% sulfuric anhydride, and oleum with a substantially higher SO_3 content than 65% may be used if available—indeed, even better results may be expected with a higher percentage of SO_3.

In some cases, the quantity of free substances, i. e., unmodified oxybenzene derivatives, in the sulfonated materials, may be substantially reduced by a vacuum distillation, but such treatment is not usually necessary. Ordinarily, for example, the sulfonated mass is simply transferred into an aqueous mixture of the aldehyde-sulfite material and there heated, preferably in a closed vessel having a suitable reflux condenser, for preparation of the ultimate product. This condensation step, which is advantageously performed in the presence of formaldehyde and sodium sulfite, is again a simple step, practicable at atmospheric pressure. To the product thus rendered water soluble (and indeed dissolved in an aqueous medium), a bleaching agent, such as sodium hydrosulfite (i. e., $Na_2S_2O_4$), is added, and after such heating as may be necessary to complete the decolorizing action, acidification (or usually merely further acidification) may then be effected to obtain the particular pH desired. Although sulfuric acid is notably convenient for this purpose, i. e., to obtain a pH of 2.5 for tanning use (it being understood that for best tanning results, the acidity should usually be within the range of pH 2.5 to 4.5), other acids may be used, for example oxalic, formic, acetic, or other acids compatible with the tanning or other treatment in which the product is employed.

The sulfonated mass and the subsequent con-

densation product (before bleaching) are usually both very dark in color, the condensation product being, for instance, dark brown or substantially black, although normally clear in the sense that it is free of detectable suspended solids. Indeed, according to my present understanding of the theory of the process—i. e., that the greater the quantity of sulfone or sulfones in the intermediate product of sulfonation, the better is the tanning action—the high sulfone content contributes particularly to the darkness of color; yet the susceptibility of the condensation product to satisfactorily complete decolorization by simple treatment, as with hydrosulfite, not only obviates any disadvantage of color darkness, but indeed cooperates to permit the use of an effectively high percentage of SO_3, with a resultant high efficiency in the sulfonation step.

Although the entire procedure is an extremely simple one, it should be appreciated that the reactions, particularly in the condensation step, may be relatively complex. As previously stated, my present belief is that the result of the sulfonation step contains the original oxybenzene derivative or derivatives in a free state, in a sulfonic acid state and in a sulfone state; exact quantitative determination of that intermediate product apparently cannot be made, nor can any exact determination be made of the chemical composition of the complex product of condensation, at least by the usual methods of anaylsis with which I am familiar. It appears, however, that the final product is not a single, simple compound (as would result from condensation, for example, of a single sulfone), and it is my belief that the new condensation product is of a complex nature wherein the constituents cooperate not only to afford the desirable tanning and other characteristics but also to effect the decolorizing treatment hereinabove described.

Although it will be understood that the procedure may be varied in a number of respects, particularly in the light of what has already been said, the following are set forth as presently preferred examples of the invention. The various quantities are stated in parts by weight.

Example 1

265 parts of phenol are sulfonated with 140 parts of 65% oleum, for approximately six hours at 160° to 170° C., the sulfonation being advantageously effected at atmospheric pressure. The resulting sulfonated mass is cooled at 100° C. and then poured into a previously prepared mixture of 660 parts of water, 330 parts of 40% formaldehyde, and 360 parts of anhydrous sodium sulfite. The complete mixture thus obtained is then heated to effect the desired condensation treatment, advantageously at substantially atmospheric pressure in a closed vessel having a suitable reflux condenser; and the treatment may be considered satisfactorily terminated when a sample is soluble in 18° Bé. sulfuric acid. To the resulting dark-colored condensation product 10 parts of anhydrous sodium hydrosulfite (i. e., $Na_2S_2O_4$, sometimes called sodium hyposulfite) are added, and heat is applied for, say, two hours, at a temperature of about 100° C. and under atmospheric pressure; whereupon the product will be found to have been suitably de-colorized for tanning purposes or the like; and for use as a tanning agent, the product after cooling may have sulfuric acid added to it unitl a pH of 2.5 is reached.

Example 2

280 parts of phenol are sulfonated with 140 parts of 65% oleum, for four hours at 160° to 170° C. The resulting mass is subjected to distillation with resulting extraction of about 50 parts of unsulfonated phenol. The mass is then cooled, as before, and added to a mixture of 450 parts water, 316 parts formaldehyde and 347 parts of anhydrous sodium sulfite. Reflux heating of this mixture, and further procedure, may be effected as in the case of Example 1.

Example 3

300 parts of cresol U. S. P. are sulfonated for ten hours at 165° to 180° C. with 140 parts of 65% oleum; and the resulting mass thereafter may be cooled and subjected to condensation and other treatment as in the case of Example 1.

Example 4

350 parts cresol U. S. P. are sulfonated for about six hours at 170° to 180° C. with 140 parts of oleum. The resulting mass may then be subjected to distillation under vacuum, for extraction of a substantial quantity of unsulfonated cresol, as in the case of Example 2, and further procedure, including the condensation step, may likewise be carried out as set forth in Example 2.

The products of the several examples have been found to possess excellent tanning properties, as previously explained. It will be understood that other oxybenzene derivatives of similar character may be employed, e. g., xylenols, or mixtures of such substances. Thus the invention is of specific practical advantage in that the process may be directly and satisfactorily carried out with ordinary commercial or "U. S. P." cresols, which usually contain some phenol and xylenol.

As stated above, improvement may sometimes be had by distilling off a part of the free phenol, cresol or the like remaining in the mass after sulfonation. It is recommended, however, that ordinarily no attempt need be made to distill off the total amount of the free material, since too great a time would be required for operation with greatest economy, and indeed, complete distillation would change the character of the mass, which is thereafter condensed with formaldehyde. To the extent that distillation may be employed, it will be understood that the temperature and vacuum (if any) for such operation may vary according to the materials (e. g., phenol, cresol or the like) used and other factors which will be recognized by those familiar with distillation procedures and apparatus. Thus in one case, for example, where the sulfonation step constituted the treatment of U. S. P. cresol with 65% oleum, satisfactory results were had by subjecting the resulting mass to distillation which began at 135° C. under a vacuum of 27 inches of mercury, and which was arrested at 155° C. Speaking generally, experience indicates that for best results the distillation temperature should never exceed 170° C.

It may be noted that better results may often be had in the bleaching or decolorizing step by the employment of higher pressures and temperatures than mentioned in the specific examples set forth above; for instance, by heating the mixture of the product with the bleaching agent for three hours under 45 pounds pressure, i. e. at 145° C.

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invention, in addition to being an excellent tanning agent, may be applied to other uses—for instance, in the tanning and textile industries, as an agent for dispersion, reserve and silk weighting. The product has been found, moreover, to constitute an excellent fungicide. An example of use as a dispersing agent is in dyeing practice, where it is desirable to break down the lumps which a powdered dyestuff tends to form upon addition to water, so that easier and quicker solution may be had. As will also be understood, a reserve is a substance which, when applied to a material to be dyed, tends to inhibit or retard subsequent dyeing at those points where application of the reserve has been made; thus, a material to which a reserve has been applied, will not take a full dyeing, but will ordinarily come out in a lighter or pastel shade.

It will be understood that the invention is not limited to the specific procedures and compositions hereinabove described, but may be carried out in other ways without departure from its spirit as defined by the following claims.

I claim:

1. The process of producing condensation products having good tanning action, which comprises subjecting material selected from the class consisting of phenol, cresol and xylenol to sulfonation under atmospheric pressure with oleum containing at least about 50% of sulfuric anhydride to produce a product containing the original material in its free state, in a sulfonic acid state and in a sulfone state, and subjecting the entire said product of said sulfonation to condensation with formaldehyde and a salt of sulfurous acid.

2. The process of producing water-soluble condensation products having good tanning action, which consists in subjecting material selected from the class consisting of phenol, cresol and xylenol to sulfonation in the presence of a high percentage of sulfuric anhydride to produce a product containing the original material in both a sulfonic acid state and in a sulfone state, said sulfonation step consisting of a single treatment performed without addition of further oxybenzene derivative material subsequent to the initiation of the step, and thereafter and without intermediate chemical treatment, and without separating the said sulfonic acid and sulfone constituents from each other, subjecting the sulfonated product to condensation with formaldehyde and a salt of sulfurous acid.

3. The process of claim 2, which includes subjecting the condensation product to decolorization by heating said product with hydrosulfite bleaching material under a pressure substantially higher than atmospheric.

4. In a process of producing water-soluble condensation products from oxybenzene derivatives wherein the oxybenzene derivative material is subjected to sulfonation and condensation, the procedure wherein the sulfonation and condensation consist of single steps performed without intermediate chemical treatment, and wherein said steps respectively comprise subjecting material selected from the class consisting of phenol, cresol and xylenol to sulfonation with oleum containing at least about 50% of sulfuric anhydride to provide a product containing the original material in the free state, in a sulfonic acid state and in a sulfone state, and subjecting the sulfonated material to condensation with formaldehyde and a salt of sulfurous acid, whereby the product of said condensation is characterized by good tanning properties, said condensation step being initiated by mixing the formaldehyde and the salt of sulfurous acid with the entire material which is treated in said step and which consists of a mixture derived from the first step and composed of the original oxybenzene derivative material in the free state, in a sulfonic acid state and in a sulfone state.

5. The process of producing water-soluble condensation products, which is initiated with a sulfonation step and is followed and terminated by a condensation step without chemical treatment intermediate said steps, and wherein said steps respectively comprise subjecting material selected from the class consisting of phenol, cresol and xylenol to sulfonation at boiling temperature and under atmospheric pressure with oleum containing at least about 65% of sulfuric anhydride to produce a mixture containing the original material in both a sulfonic acid state and a sulfone state, and subjecting the mixed sulfonic acid material and sulfone material, without separating said sulfonic acid and sulfone materials from each other, to condensation at boiling temperature and under atmospheric pressure with formaldehyde and sodium sulfite.

6. The process of producing condensation products which consists in: subjecting material selected from the class consisting of phenol, cresol and xylenol to sulfonation under atmospheric pressure with oleum containing at least about 50% of sulfuric anhydride, the oleum constituting about 30% or more by weight of the mixture of the material and oleum; and thereafter subjecting the entire product of the aforesaid sulfonation step, without separating any constituent therefrom, to condensation with formaldehyde and a salt of surfurous acid.

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