SYNTHETIC TANNING AGENTS FOR PRODUCING SHRUNKEN GRAIN LEATHER

Stanley A. Lipowski, Livingston, N.J., assignor to Diamond Shamrock Corporation, a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A water soluble shrunken grain synthetic tanning agent in substantially monomeric form is obtained by reaction of a dihydroxy diphenyl sulfone, formaldehyde and naphthalene sulfonic acid in aqueous solution. Molar proportions of reactants are selected to obtain a reaction product having at least 0.5 free methylol groups per mole of sulfone. Reactant excess is provided and represent a large excess of formaldehyde, of from about 20° C. to about 150° C. until a clear solution is obtained.

The present invention relates to synthetic tanning agents for producing shrunken grain leather and the processes for producing and using such synthetic tanning agents.

Shrunken grain leather is a type of leather which has a pattern developed on the hide by the action of the tanning agent. The shrinking action is most pronounced on the grain of the leather which is the most sensitive part of the hide. The shrinking effect is visible on all of the corium of the hide and is characterized by a decrease in the total area of the hide. The shrunken grain pattern formed on the surface of leather by action of tanning agents is quite different from the pattern obtained by simple embossing. The pattern formed by shrinking the grain of the skin by tanning has a natural look contrary to the pattern obtained by simple embossing which has a definite artificial look and very little eye appeal. The principal problem in producing a shrunken grain effect on the skins or hides which are to be used for manufacturing shoe leather or other fashion leathers is to obtain a natural looking pattern uniformly distributed over all of the surface area. Furthermore, such pattern should have sufficient depth and permanent features that the shrunken grain pattern will completely recover its appearance after the leather has been placed and the stretch has been released. Synthetic tanning agents employed in producing shrunken grain leathers besides effecting the shrinking of the grain must be complete and satisfactory tanning agents for the leather and not impair the generally required standards of good grade upper leather. Such standards mean that the shrunken grain leather must have good round feel, high tensile strength, high stitch tear strength and the like.

Numerous attempts have been made in the prior art to produce a synthetic shrunken grain tanning agent which will meet all of the above requirements. However, none of the synthetic tanning agents developed to date has been completely satisfactory. The principal reasons for the difficulties which have been encountered in the development of synthetic tanning agents for producing shrunken grain leathers are that any good synthetic tanning agent under proper management of tanning processes can produce a shrinking effect on a skin or hide but none of the previously developed synthetic tanning agents have been able to satisfy all of the requirements that must be met in producing a satisfactory shrunken grain leather. Such agents generally produce shrunken grain leather having a wild coarse grain, that is, the grain is highly irregular. Furthermore, the shrunken grain pattern is not uniform and does not completely cover the entire surface area of the hide. The pattern has low depth and poor recovery on stretch which means that the shrunken grain leather may superficially look satisfactory but when it is exposed to the drastic action of shoe manufacturing machines and the like, the shrunken grain leather will partly or entirely lose its pattern. Since a shrunken grain leather must maintain its pattern during manufacture as well as during use, it is extremely important that the pattern has good recovery after stretching or use.

Production of satisfactory shrunken grain leather is highly advantageous in tannery operations where shoe leather or other fashion leathers are being produced. In every tannery producing smooth upper grade leather, some of the stock is of poor quality and produces second grade leather. Such second grade leather results from natural defects in the skins or hides such as barbed wire scratches, skin defects caused by insect bites, brand marks, other injuries or defects. These defects are clearly visible in the finished leather, limit the usefulness of the finished leather and in the cutting area. Obviously, second grade leather and products produced from second grade leather must be sold at much lower prices. For a long time, it has been a major problem of upper leather tanners to find more effective methods to utilize the defective hides more to their advantage. Such defective hides can be more effectively utilized when they are turned into other hides at some intermediate step in the tanning operation such as after liming or pickling or preferentially in the blue, that is, after chrome tanning when the defects in the hides become more apparent. If the defective hides are separated at such a point and then converted to shrunken grain leather with all of its desirable properties, the shrunken grain leathers can be sold as highly profitable fashion leathers. Furthermore, such defective hides are not converted to smooth upper leather with the attendant losses in the cutting area. It is to be understood that effective utilization of defective hides in the production of shrunken grain leathers can be accomplished only if the shrinking effect obtained is of such a nature that it provides extremely good coverage of all of the defects in the hide and gives a leather which has a natural appearance, that is, distinctly different from the appearance of cheap embossed leather. Only a few of the synthetic tanning agents suggested by the prior art have shown promise in the production of shrunken grain leather. Although these agents have been able to produce more or less visible shrinking effects, none of these agents has been able to meet all of the rigorous requirements for shrunken grain leather outlined above.

For example, a synthetic tanning agent is disclosed in U.S. Patent No. 3,010,779 as being useful in the production of shrunken grain leather. This synthetic tanning agent is based on a 4,4'-dihydroxy diphenyl sulfone resin condensed with naphthalene sulfonic acid and formaldehyde and is in a very strong acid form, that is, the agent contains free sulfuric acid and other strong acids which are extremely injurious to leather. This agent cannot be neutralized to the pH range of about 8 to 11 and the amount normally used in tanning processes because the agent precipitates from solution during neutralization. The net result is that this agent produces a shrinking effect on leather which is of a very low quality and the pattern is coarse and not complete. The poor action of this synthetic tanning agent can be attributed to several factors. The agent lacks free methylol groups, that is, unreacted methylol groups which provide the astringency required to shrink the grain surface. The agent has low salt tolerance, that is, it precipitates in salt solutions containing low salt concentrations, that is, solutions containing as little as 1% by weight of sodium chloride. Thus, this agent on contact with pickled stock which contains appreciable quantities of salt will precipitate at an early stage during the tanning operation so that its shrinking action on the grain will be lost.
Precipitation from salt solutions at these concentrations indicates that the agent is a polymeric material. Consequently, this agent is only able to act as a tanning agent because it does not have sufficient astringency to cause proper shrinking of the grain surface. Similar results have been obtained with other synthetic tanning agents in which the agents are excellent tanning agents but do not have sufficient astringency to cause rapid shrinking of the grain before further penetration of the synthetic tanning agent into the leather makes shrinking of the grain surface impossible.

It is an object of the present invention to provide synthetic tanning agents which will produce shrunk grain leathers which have deep, fine and uniform patterns, evenly distributed over the entire surface of the leather, have good recovery after stretching and have the other requirements of high fashion leathers. Another object of the present invention is to develop processes for producing synthetic tanning agents for use in the production of shrunk grain leathers. A further object is to produce tanning processes employing such agents in the production of shrunk grain leathers. Still another object is to produce shrunk grain leathers. Other objects of this invention will become apparent from the detailed description given hereinafter.

It is intended that the detailed description and specific examples do not limit the present invention but merely indicate preferred embodiments thereof since various changes and modifications within the scope of the invention will become apparent to those skilled in the art.

The above as well as other objects of the present invention have been most unexpectedly and successfully achieved in the following manner. I have discovered a new and not previously class of water soluble synthetic tanning agents which are useful in producing shrunk grain leathers for use in upper shoe leather and other high fashion leathers. Furthermore, I have discovered processes for producing such synthetic tanning agents. Additionally, I have found that use of these synthetic tanning agents in the tanning of hides and skins consistently produce high quality upper shrunk grain shoe leathers, fashion leathers and the like which far exceed the shrunk grain leathers produced in the past.

I have found that such synthetic tanning agents must contain at least 0.5 free methylol groups per mole of sulfone employed, that is, the unreacted methylol groups per mole of sulfone present in the synthetic tanning agent if all of the desirable properties are to be obtained with the agent in the production of shrunk grain leathers. Furthermore, I have discovered that it is essential for the tanning agent to be substantially in monomeric form and that synthetic tanning agents based on polymeric forms or resins are to be avoided. Such polymeric agents have poor shrinking action on leather. I have also found that such tanning agents when in solution should not precipitate on neutralization at pHs from about 0 to about 7.

Such tanning agents can be neutralized with alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and the like, ammonium hydroxide, low molecular weight amines such as monomethylamine, dimethylamine, monoethanolamine, diethanolamine, triethanolamine, n-ethylamine, n-propylamine, their isomers and the like. Likewise, such tanning agents should not contain strong acids such as free sulfuric acid or the like. Furthermore, such tanning agent should be soluble in tanning solutions or liquors containing at least 2.5% by weight of sodium chloride. The importance of such structural, chemical and physical requirements in synthetic tanning agents for use in the production of shrunk grain leathers was not appreciated or suggested by the prior art.

Briefly, the synthetic tanning agents disclosed in the present invention are the reaction products of one mole of a sulfone having a purity of from about 95% to 100% by weight such as 4,4'-dihydroxy diphenyl sulfone, 4,2'-dihydroxy diphenyl sulfone, 2,2'-dihydroxy diphenyl sulfone or mixtures of these sulfones with from about 0.5 mole to about 5.0 moles of formaldehyde or formaldehyde liberating compositions per mole of sulfone and from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of sulfone with the proviso that the final reaction product contains at least 0.5 free methylol groups per mole of sulfone, that is, unreacted methylol groups per mole of sulfone employed, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7. Such synthetic tanning agents can also be the reaction products of (a) one mole of methylolated sulfone having a purity of from about 95% to 100% by weight such as methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 4,2'-dihydroxy diphenyl sulfone, methylolated 2,2'-dihydroxy diphenyl sulfone or their mixtures wherein one mole of the sulfone contains from about 1.5 to about 4 free methylol groups and (b) from about 0.5 to about 2.0 moles of 2-naphthalene sulfonic acid per mole of sulfone with the proviso that final reaction product contains at least 0.5 free methylol groups per mole of sulfone employed, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7.

These water soluble shrunk grain synthetic tanning agents can be prepared by reacting together at a temperature range of from about room temperature to about reflow temperature, an aqueous reaction mixture containing one mole of a sulfone having a purity of from about 95% to 100% by weight selected from the group consisting of 4,4'-dihydroxy diphenyl sulfone, 4,2'-dihydroxy diphenyl sulfone, 2,2'-dihydroxy diphenyl sulfone or their mixtures, from about 1.5 moles to about 5.0 moles of formaldehyde or a formaldehyde liberating composition per mole of sulfone, from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of sulfone and water with the proviso that the quantities of sulfone, aldehyde and 2-naphthalene sulfonic acid are selected within the molar range stated so that the final reaction product contains at least 0.5 free methylol groups per mole of sulfone, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7. Such products should contain little, if any, unreacted naphthalene sulfonic acid. The temperature employed in this process may vary from about 20°C. to about 110°C. and may be employed as may be necessary to develop the desired characteristics of the final product. The temperature of the reaction mixture is usually between 95°C. and 110°C. at atmospheric pressure. The mixture is refluxed until a clear solution is obtained and the product has the following properties.

The final reaction product must contain at least 0.5 free methylol groups per mole of sulfone employed. Furthermore, substantially all of the formaldehyde should be condensed with the methylolated sulfone. The final product should be soluble in salt solutions containing at least 2.5% by weight of sodium chloride. Furthermore, the final product should not precipitate from solution on neutralization at pHs from about 0 to about 7. The final product should be sufficiently neutralized so that it does not contain strong acids such as free sulfuric acid or the like. When the final product has the above properties,
it is then cooled to room temperature. The procedure described above avoids bridging between dihydroxy diphenyl sulfone molecules, other reactants or the final product by reactions with formaldehyde which will produce polymeric materials. When desired, a solvent such as alcohol or any other solvent that does not interfere with the reactions involved in the process may be used in conjunction with water. Use of such solvent mixtures can be advantageous when higher or lower reflux temperatures are desired.

Alternatively, these water soluble shrunked grain synthetic tannings agents can be prepared by reacting together at a temperature range of from about 30° to about 40° C. a formaldehyde solution containing one mole of a methylated sulfone having a purity of from about 95% to 100% by weight such as methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 4,2'-dihydroxy diphenyl sulfone, methylolated 2,2'-dihydroxy diphenyl sulfone or their mixtures wherein the sulfone contains from about 1.5 to about 4 free methylol groups per mole of sulfone employed, from about 0.5 mole to about 2.0 mole of 2-naphthalene sulfonic acid per mole of sulfone and water with the proviso that the quantities of methylolated sulfone and 2-naphthalene sulfonic acid are selected within the molar ranges stated so that the tannin agent containing at least 0.5% free methylol groups or reaction mixture containing of methylolated sulfone employed, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7. The quantity of water employed in this process may vary. Usually from about one and one-half to about two times the weight of sulfone of water is employed in the methylolation step and from about one-half to about two times the weight of the sulfone of water is employed in the condensation process. The heating of the reaction mixture at the aforementioned temperatures, or preferably at reflux temperature, that is, about 95° C. to about 110° C. is carried out until a clear solution is obtained. If desired, the condensation can be carried out under pressure or in the presence of solvents at temperatures as high as about 150° C. The reaction product, that is, the water soluble shrunked grain synthetic tanning agent should have the following properties. The final reaction product must contain at least 0.5 free methylol groups per mole of sulfone employed. Furthermore, substantially all of the naphthalene sulfonic acid should be condensed with the methylolated sulfone. The reaction product should be soluble in salt solutions containing at least 2.5% by weight of sodium chloride. Further, the reaction product should not precipitate from solution on neutralization at pHs from about 0 to about 7. The final product should be sufficiently neutralized so it does not contain strong acids such as free sulfuric acid or the like.

The number of free methylol groups per mole of sulfone in either the dimethylolated sulfone or the synthetic tanning agents described above can be determined by the De Jong method which is described in Rec. trav. chim., 72: 653, 654 (1953).

Methylolation of the sulfone

Methylolation of the sulfone can be achieved in the following procedure which avoids bridging between dihydroxy diphenyl sulfone molecules during methylolation. When bridging occurs, the resulting polymeric materials are partially methylolated sulfone resins, which on acidification separate as gummy materials and are not easy to separate easily by precipitation and washed by decantation. Prior to methylolation, the dihydroxy diphenyl sulfone is reacted with sodium hydroxide in such proportions that both of the hydroxyl groups in the phenol rings are converted to the corresponding sodium salts. At this point, the sulfone should be water soluble and have a pH of from about 9.5 to about 10.0. The disodium salt of the sulfone is then reacted with sufficient formaldehyde to obtain the desired methylolated sulfone. Usually from about 1.5 moles to about 5.0 moles of formaldehyde or a formaldehyde liberating composition per mole of sulfone is employed. Methylolation takes place at moderate temperatures such as about 20° C. to about 55° C. over an extended period of time. For example, methylolation at about 45° C. to about 55° C. will require from about 16.5 hours to about 30 hours. The methylolation remaining in the mixture can be analyzed by determining the amount of formaldehyde remaining in the mixture by the method described in Example III below. This method determines the amount of formaldehyde remaining in the reaction mixture after methylolation. The methylolation reaction mixture can also be analyzed by the De Jong method described above. The De Jong method determines the number of free methylol groups present in the methylolated sulfone. When the De Jong method is employed, the unmethylolated formaldehyde should be removed from the reaction mixture after the number of methylol groups per mole of sulfone is determined. After methylolation is complete, the methylolated dihydroxy diphenyl sulfone is recovered in the form of a solid precipitate by precipitation with an acid such as hydrochloric, sulfuric or the like. The solids formed during the acidification are washed with water free of free materials and easily removed from the methylolated dihydroxy diphenyl sulfone precipitate by simple decantation and washing. After the methylolated sulfone has been separated from the reaction mixture as a solid and washed free of salts, unretracted formaldehyde, formaldehyde liberating compositions and the like, it is reacted in aqueous solution with the required quantity of 2-naphthalene sulfonic acid at a temperature of about 55° C. to about 150° C. to obtain a synthetic tanning agent having the properties described above. The methylolated sulfone to be used in the present invention should have a purity of about 95% by weight to 100% by weight and should contain from about 0.5 to about 4 free methylol groups per mole of sulfone employed. The methylolated sulfone may be methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 4,2'-dihydroxy diphenyl sulfone, 2,2'-dihydroxy diphenyl sulfone or mixtures thereof. The impurities in the methylolated sulfone include methylolated polymeric sulfones, methylolated phenol sulfonic acid, other by-products and the like.

The dihydroxy diphenyl sulfone or mixture of sulfones employed in the processes disclosed in this invention must be of high purity. It should have a purity of about 95% to 100% by weight of 4,4'-dihydroxy diphenyl sulfone, 4,2'-dihydroxy diphenyl sulfone, 2,2'-dihydroxy diphenyl sulfone or their mixtures and should not contain more than 5% by weight of impurities such as polymeric sulfones, phenol sulfonic acids, other byproducts or the like. A procedure for preparing a dihydroxy diphenyl sulfone having satisfactory properties is described in Example I below. It is to be understood that any known method which produces dihydroxy diphenyl sulfone resins or mixtures thereof having purities from about 95% to about 100% by weight for use in the present invention.

Formaldehyde or formaldehyde liberating compositions can be used in the preparation of the synthetic tanning agents and methylolated sulfones disclosed in the present invention. For example, formaldehyde can be used in the form of 10% to 40% aqueous solutions, 30% to 55% alcoholic solutions with solids such as methanol, n-butanol, l-butanol or the like. Formaldehyde can also be used in the form of a formaldehyde liberating composition such as its polymeric forms such as parafomaldehyde, trioxane, or the like. It is also to be understood that such formaldehyde liberating compositions include any form such as an acetal which is capable of producing formaldehyde such as acetals and the like.
The synthetic tanning agents and their use

The synthetic tanning agents produced by the processes described above are analyzed by the De Jong method referred to above to determine if they contain at least 0.5 mole of free methylol groups per mole of sulfone employed. When desired, the tanning agents may contain as many as 3 free methylol groups per mole of sulfone employed in the process. Furthermore, the tanning agent should be neutralized to the point where all of the free sulfonic acid present in the naphthelene sulfonic acid employed in the process is completely neutralized and any free, unreacted 2-naphthene sulfonic acid remaining in the synthetic tanning agent is present only in an amount sufficient to give a pH of from about 0 to about 7 in the finished synthetic tanning agent. For most purposes, about 90% of the 2-naphthene sulfonic acid groups, after reaction of the naphthelene sulfonic acid with the methylolated dihydroxy diphenyl sulfone, are neutralized. The presence of unneutralized sulfonic acid or other sources of high acidity in the finished synthetic tanning agent is highly undesirable because such activity contributes substantially to the coarseness of the pattern produced when the synthetic tanning agent is employed in shrunken grain tanning. Furthermore, the synthetic tanning agents produced by the processes disclosed in this invention should be soluble in water at any dilution, soluble in salt solutions containing at least 2.5% by weight of sodium chloride. Likewise, the tanning agent should not precipitate from solutions on neutralization to pH of from about 0 to about 7.

The synthetic tanning agents disclosed in this invention are useful in producing shrunken grain effects on animal skins such as cowhides, calfskins, goatskins, horsehides, reptile skins, other animal skins or the like. The term skin is used to include any animal skin or hide which can be used in the production of shrunken grain leather. As examples of skins which may be employed in the production of shrunken grain leather, there may be mentioned skins of freshly killed animals, limed skins, pickled skins, partly tanned skins, partly dechromed skins, dechromed skins and the like. Generally from about 15% by weight to about 50% by weight based on the weight of the skins of the synthetic tanning agent is employed. By the term synthetic tanning agent is meant the solution of the solid reaction products, salts and the like obtained by the processes disclosed in this invention. The synthetic tanning agent generally contains from about 15% by weight to about 50% by weight of solid reaction products. Usually from about 30% by weight to about 100% by weight based on the weight of skins or hides of water is added to the synthetic tanning agent solution to prepare the tanning solution or liquor. Shrunken grain leathers are produced by drumming the synthetic tanning agent into the animal skin. The synthetic agent is used in form of a solution or liquor and is drummed into the skin at a temperature of from about 70° to about 90° F. for about two hours to about twelve hours. Exhaust of the synthetic tanning agent from the tanning solution or liquor at the end of the drumming process is essentially complete, that is, the tanning agent is absorbed in the skin and little if any of the tanning agent remains in the tanning solution or liquor.

Shrunken grain leather produced by synthetic tanning agents disclosed in this invention can be used in the manufacture of upper shoe leather, garment leather, handbag leather, high fashion leather and the like. When the synthetic tanning agents are used in connection with vegetable tannages, moccasin type leather can be produced. The synthetic tanning agents of this invention can be combined not only with chrome tannages but with other tannages such as zirconium tannages and the like. When chrome stock is used in the production of shrunken grain leathers, the leather is dechromed prior to use. The dechroming process can be varied over wide limits by using chemicals and/or materials which complex with chromium and facilitate its removal from the chrome tanned leather.

Materials useful in dechroming leather include complexing acids such as oxalic, tartaric, citric, phosphoric acid or salts of such acids, e.g., Rochelle salt and the like, chelating agents such as ethylenediaminetetraacetic acid, hydroxamic acids, amidoximes or the like. Such dechroming agents are applied in sufficient quantities to dechrome the stock to the point where its shrinkage temperature in boiling water drops from about 212° F. to about 110° F. Preparing conditions employed during dechroming must be controlled carefully so that the internal structure of the leather is not damaged. After the leather is dechromed, the stock must be promptly washed with salt water to avoid acid swelling. The resulting washed dechromed stock is then used in the shrunken grain process in the same manner as pickled skins or other forms of stock.

When the tanning agents of the present invention are employed in the production of shrunken grain leathers, the mechanical action encountered in the drumming and other plant operations which promote the shrinkage effect of the synthetic tanning agents must be controlled carefully. For example, the speed of the drums must not be exaggerated in order to prevent overheating of the stock. The temperature during the shrinking process must be carefully controlled and kept as low as possible. Usually temperatures in the range of from about 70° F. to about 90° F. are employed. The rotating drums must be stopped at certain time intervals during the process so that they can be aired off and allowed to cool before the temperature of the stock reaches the critical upper temperature limit of about 90° F. Extensive damage can be done to the stock which will render it useless as leather unless these precautions are taken. The amount of synthetic tanning agent solutions employed in shrunken grain tanning will be from about 15% to about 50% by weight (as is) based on the weight of the stock.

Shrunken grain leather obtained by the processes disclosed in this invention shows undiminished strength after it is rechromed. The shrunken grain leather can be rechromed with from about 1½ to about 2½% chromic oxide based upon the weight of the stock. The starting basicity during rechroming can be as low as 33% to 50% Schollemmer degrees which corresponds to a basicity of 4/12 to 6/12. The lower basicity chrome liquors can be subsequently made more basic by the addition of alkalies such as sodium bicarbonate, ammonium bicarbonate or the like. Although higher basicity liquors do not require basicity adjustments, their action is more drastic and their use must be avoided if important that care is taken not to overheat the stock during the rechroming process. The short floats and high basicity of the liquors in conjunction with the mechanical action of the rotating drums can easily cause severe damage to the hides in rechroming if the stock temperature is permitted to rise above temperatures of about 90° F. or higher. Generally, the shrunken grain stock is rechromed to a point where its shrinkage point is brought up to a minimum temperature of about 205° F. Generally, shrinkage temperatures of from about 210° F. to about 212° F. are the most desirable.

When stock such as pickled stock or dechromed stock is tanned with the synthetic tanning agents of this invention, complete exhaust of the synthetic tanning agent is observed. Complete exhaust demonstrates the high affinity which the tanning agent has for the hide substance. Spent liquors from shrunken grain tanning processes in which the synthetic tanning agents of this invention are used contain little if any of the tanning agents. This is highly desirable as little if any of the agents are lost during the tanning processes. The concentration of synthetic tanning agents in the spent liquors can be determined by conventional methods such as the Official Hide Powder Method and the like.

For a fuller understanding of the nature and objects of this invention, reference may be made to the following examples which are given merely to illustrate the inven-
tion and are not to be construed in a limiting sense. All weights, proportions and percentages are by weight unless otherwise indicated. Likewise all temperatures are °C, unless otherwise indicated.

**EXAMPLE I**

(A) Preparation of a dihydroxy diphenyl sulfone

1148 g. (12.2 moles) of phenol, 612 g. (6 moles) of sulfuric acid (96% by weight active) and 125 g. monochlorobenzene were charged into a reaction vessel equipped with an agitator and a water separation trap. The reaction mixture was heated to the reflux temperature which was about 140° C. The escaping vapors of chlorobenzene and water formed during the reaction were condensed in the condenser and were separated in the water trap. The dry chlorobenzene was returned to the reaction mixture. Reaction temperature was gradually increased to a temperature between 165° C. and 170° C. After from about 210 cc. to 215 cc. of water had been separated by azeotropic distillation, the reaction mixture was titrated to determine its acidity. A 10 g. sample of the reaction mixture at this point should not require more than 19.00 cc. to 20.00 cc. of 0.5 N sodium hydroxide solution to neutralize the sample to a pH of 7.0. This test showed that over 75 percent of the reactants have been converted to dihydroxy diphenyl sulfone. Higher conversion would require ten to fifteen hours and longer times with the resulting resinsification of the sulfone. Tilters in above mentioned range have been found to be satisfactory in that they avoid resinsification and provide satisfactory conversions to dihydroxy diphenyl sulfones.

After the desired acidity was obtained, 500 cc. of water was added carefully to the reaction mixture. The reaction product was then neutralized to a pH between 5 and 6 by the cautious addition of from about 120 g. to about 130 g. of 50% by weight sodium hydroxide solution. Approximately 1,000 cc. of water was then added to the reaction product and the resulting mixture was azeotropically distilled to remove the chlorobenzene. The chlorobenzene was removed from the water and the water returned to the reaction mixture. After all of the chlorobenzene was stripped from the reaction mixture, an additional 1,000 cc. of water was added and the resulting solution of the reaction product was heated to its boiling point. A clear solution was obtained at the boiling point. The solution contained the reaction product dissolved in about 2,500 cc. of boiling water.

The clear solution was then transferred to a reaction vessel equipped with an approximately 4,000 cc. of boiling vessel and the resulting diluted solution was allowed to cool slowly to room temperature with vigorous agitation. Dihydroxy diphenyl sulfone precipitated in the form of cream colored crystals from the solution on cooling to room temperature. The crystals were recovered by filtration or centrifugation or were left in the crystallization vessel and were then washed several times with cold water until the crystals were free of residual salts. The resulting dihydroxy diphenyl sulfone crystals were then either dried or left in the form of a wet paste for use in further reactions. The dihydroxy diphenyl sulfone crystals were analyzed for isomer distribution by the procedure given in Example I of U.S. Patent No. 2,833,828—Saals (May 6, 1958). The crystals were found to have a purity of 98% by weight and a weight ratio of 88% of 4,4'-dihydroxy diphenyl sulfone isomer to 12% of 4,2'-dihydroxy diphenyl sulfone. The 2% by weight of impurities in the mixture consisted of polymeric sulfones, phenol sulfonic acids, other byproducts and the like.

(B) Recrystallization of dihydroxy diphenyl sulfone

When desired or required, the crystalline dihydroxy diphenyl sulfone isomer mixture obtained in part (A) above was further purified by the following procedure. The crystalline material was suspended in twenty times its weight of water and heated to the boiling point. The crystalline material dissolved at the boiling point and a clear solution was obtained. 0.1% by weight of decolorizing carbon and 0.5% by weight of filter aid were added to the boiling mixture. The mixture was then stirred for about five minutes and filtered at its boiling point to remove the decolorizing carbon, filter aid and other impurities. The clear, decolorized solution of dihydroxy diphenyl sulfone isomers was then cooled slowly to room temperature with vigorous agitation. Crystals of the dihydroxy diphenyl sulfone isomers separated on cooling to room temperature and were removed by filtration. The recrystallized dihydroxy diphenyl sulfone isomer mixture was in the form of pure white crystals. It was approximately 100% by weight pure. The isomers were present in a weight ratio of 88% of the 4,4'-dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-dihydroxy diphenyl sulfone isomer. It is to be understood that purification of the dihydroxy diphenyl sulfone by recrystallization is not generally required in the preparation of the synthetic tanning agents of this invention for most tanning processes.

**EXAMPLE II**

Preparation of a 2-naphthalene sulfonic acid solution

128 g. (1 mole) of naphthalene and 160 g. (1.6 moles) of sulfuric acid (98% by weight active) were mixed together in a reaction vessel at room temperature. The resulting reaction mixture was heated rapidly to 150° C. and agitated for three hours at 115° C. The resulting reaction product which was a mixture of 2-naphthalene sulfonic acid and sulfuric acid was cooled to 80° C. and sufficient cold water was added to obtain a 2-naphthalene sulfonic acid-sulfuric acid mixture having an activity of about 75% by weight. This mixture was then cooled to room temperature. The mixture contained one mole of 2-naphthalene sulfonic acid and 0.6 mole of sulfuric acid.

**EXAMPLE III**

Preparation of a synthetic tanning agent

159 g. of a dry crystalline dihydroxy diphenyl sulfone isomer mixture, containing 98% by weight of sulfones having an isomer weight ratio of 88% of the 4,4'-dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-dihydroxy diphenyl sulfone isomer and 2% by weight of impurities consisting of polymeric sulfones, phenol sulfonic acids, other byproducts and the like as described in part (A) of Example I above, 156 g. water and 100 g. (1.25 moles) of 50% by weight sodium hydroxide solution were mixed together and heated until a clear solution was obtained. The mixture of sulfone isomers used in this example weighed 156 g. (0.625 moles). The resulting clear solution was cooled to about 50° C. and 106 g. (1.307 moles) of formaldehyde (37% by weight active) was added. The molar ratio of formaldehyde to dihydroxy diphenyl sulfone was 1.307/0.625 or 2.09. This reaction mixture was stirred at a constant temperature of 50° C. for 24 hours. As reaction proceeded, the initially clear solution became milky in appearance.

After reaction for 24 hours at 50° C., a sample of the reaction mixture was titrated by a modified sodium bisulfite method to determine its formaldehyde content. Briefly, this method involved addition of a 5 g. sample of the reaction mixture to 50 cc. of a 10% by weight sodium chloride solution. Sulfuric acid (98% by weight active) was then added to obtain a pH of about 5. A precipitate formed and was removed by filtration. The filtrate was collected and then neutralized to a pH of 7.0, 50 cc. of 1 M sodium sulfite solution was added. When formaldehyde was present in the filtrate, the pH of the filtrate was above 9. The filtrate was then backtitrated with 0.5 N hydrochloric acid solution to a pH of 9.0. When formaldehyde was not present, the pH of the filtrate after bisulfite addition was 9 and backtitration with 0.5 N hydrochloric acid was not required.
The percentage of formaldehyde present in the filtrate was then calculated by the following formula:

\[
\text{Percent formaldehyde} = \frac{\text{cc. HCl} \times \text{normality} \times 3.008}{\text{weight of sample}}
\]

wherein cc. HCl represents the quantity of 0.5 N hydrochloric acid required to back-titrate to a pH of 9. The formaldehyde content of the preparation described in this example was found to be 1.65% by weight. The concentration of formaldehyde present initially in the reaction mixture was 7.53% by weight which means that 5.88% by weight of formaldehyde or 78.1% of the total formaldehyde employed initially in the reaction reacted. This formaldehyde usage meant that 1.02 moles of formaldehyde reacted with the phenolic rings present in the dihydroxy diphenyl sulfone, or in other words, the ratio of free methylol groups per mole of dihydroxy diphenyl sulfone was 1.63 free methylol groups per mole of dihydroxy diphenyl sulfone.

After the formaldehyde analysis, the reaction mixture was cooled to about 10° C. 230 cc. of cold water and 190 g. of sulfonic acid (33.5% by weight active) were added with cooling. The resulting mixture which contained a precipitate of methylolated dihydroxy diphenyl sulfone in a water and salt solution was decanted to remove the solution of water, unreacted formaldehyde and salt formed during the reaction. The precipitated dihydroxy diphenyl sulfone crystals were then washed three times with 600 cc. portions of cold water and each cold water wash was removed by decantation. The formaldehyde content of the wash water obtained from the third wash and decantation was analyzed by the procedure described above and found to be 0.0% by weight. The pH of the third wash water was 5.4. After all of the formaldehyde had been removed by washing, the number of methylolated groups per mole of sulfone in the methylolated sulfone crystals was determined by the De Jong method as described in Rec. trav. Chim. 72: 653, 654 (1953). The methylolated sulfone was found to contain 1.6 free methylol groups per mole of sulfone. The reaction mixture was 98% by weight pure and contained 2% by weight impurities. The weight ratio of isomers in the crystals was 88% of methylolated 4,4'-dihydroxy diphenyl sulfone to 12% of methylolated 4,4'-dihydroxy diphenyl sulfone isomers. The 2% by weight of impurities included methylolated polymeric sulfones, methylolated phenol sulfonic acids, other byproducts and the like.

247.5 g. of 2-naphthalene sulfonic acid mixture (about 75% by weight active) which contained 0.71 mole of 2-naphthalene sulfonic acid and was prepared by the procedure described in Example II above and 25 cc. of water were added to the wet, washed methylolated dihydroxy diphenyl sulfone crystals obtained above. The resulting reaction mixture was heated to reflux. Reflux temperature was about 110° C. After heating for five hours at reflux 400 cc. of cold water was then added to the reaction mixture and the mixture neutralized under cooling by the addition of 105 g. of 50% by weight sodium carbonate solution. The resulting neutralized solution was slightly hazy. 35 g. of isopropyl alcohol was added and the solution cleared immediately. The pH of the clear solution was 2.2 as is. The solution, which was a synthetic tanning agent, contained 34.5% by weight of solids. The pH of the solution when diluted with distilled water to 1% by weight solids was 4.4. The solution, which contained 34.5% by weight solids, was soluble at all proportions in water and was soluble in a 2.5% by weight sodium chloride solution. Furthermore, the agent did not precipitate from solution on neutralization at pHs between about 0 and about 7. The number of free methylol groups in the synthetic tanning agent as determined by the above-mentioned De Jong method was found to be 0.6 free methylol group per mole of sulfone employed in the agent.

154 g. of a dicyclohexyl diphenyl sulfone paste mixture prepared by the procedure described in part (A) of Example I above was mixed with 85 g. of water and 75 g. (0.94 mole) of 50% by weight sodium hydroxide solution and heated until a clear solution was obtained. 114 g. (1.41 moles) of formaldehyde solution 37% by weight was added at 50° C. and the mixture was stirred at 50° C. for 24 hours. The sulfone paste employed in this example contained 78% by weight of solids, the solids being 98% by weight of a mixture of pure sulfone isomers and 2% by weight of impurities. The mixture of sulfone isomers weighed 0.175 g. (0.47 mole). The sulfone isomers in the mixture were present in a weight ratio of 88% of the 4,4'-dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-dihydroxy diphenyl sulfone isomer. The 2% by weight of impurities in the mixture consisted of polymeric sulfones, phenol sulfonic acids, other byproducts and the like. The molar ratio of formaldehyde to dihydroxy diphenyl sulfone in this reaction mixture was 3 moles of formaldehyde to 1 mole of dihydroxy diphenyl sulfone. After reaction for 24 hours at 50° C., a sample of the reaction mixture was titrated for its formaldehyde content by the procedure described in Example III above and found to contain 2.23% by weight of unreacted formaldehyde. The initial formaldehyde content of the reaction mixture was 9.95% by weight. In other words, 7.7% by weight of formaldehyde, which represented 77.6% of the total amount of formaldehyde used was consumed in the reaction. This formaldehyde usage represented reaction of 1.09 moles of formaldehyde with 0.47 mole of dihydroxy diphenyl sulfone, that is, the formaldehyde reacted with the phenolic rings present in the sulfone. The ratio of free methylol groups to moles of dihydroxy diphenyl sulfone was 2.52 free methylol groups per mole of dihydroxy diphenyl sulfone. After methylation, 200 cc. of cold water was added to the reaction mixture and the reaction mixture was cooled to 10° C. A solution containing 50 g. of sulfuric acid (96% by weight active) and 100 g. of water was added to the reaction mixture with good cooling. The methylolated dihydroxy diphenyl sulfone separated from the reaction mixture on cooling to 10° C. and the resulting slurry contained crystals of the methylolated dihydroxy diphenyl sulfone and a solution of unreacted formaldehyde, salt and other impurities. The slurry was filtered and the crystals washed with 50 g. of 2-naphthalene sulfonic acid mixture allowed to settle. The solution containing the impurities was removed from the crystals by decantation. The crystals of methylolated dihydroxy diphenyl sulfone were then washed three times with 500 cc. portions of cold water. The slurry was externally cooled with ice during washing and decantation. After each addition of wash water, the crystals were slurried, allowed to settle and the wash water was decanted from the cooled slurry. The formaldehyde content of the last wash water was analyzed by the procedure described in Example III above and found to be 0.0%. The pH of the last wash water was 3.8. The washed methylolated sulfone crystals were analyzed by the above described De Jong method and found to contain 2.32 free methylol groups per mole of sulfone. The crystals were found to be 98% by weight pure and to contain 2% by weight of impurities. The weight ratio of the isomers in the crystals was 88% of methylolated 4,4'-dihydroxy diphenyl sulfone to 12% of methylolated 4,2'-dihydroxy diphenyl sulfone. The 2% by weight of impurities in the crystals consisted of methylolated polymeric sulfones, methylolated phenol sulfonic acids, other byproducts and the like.

187.5 g. of 2-naphthalene sulfonic acid mixture (about 75% by weight active) which contained 0.54 mole of 2-naphthalene sulfonic acid and was prepared by the procedure given in Example II above, and 9 g. of water
were added to the washed methylolated dihydroxy diphenyl sulfone crystals and the resulting reaction mixture was refluxed for 5 hours at about 110°C. After refluxing for five hours, the reaction mixture was cooled to room temperature. 250 cc. of water was then added to the cooled mixture and the mixture was neutralized to a pH of 2.5 with 80 g. of 50% by weight sodium hydroxide solution. The resulting product was a shrunk grain synthetic tanning agent in the form of a light yellow colored clear syrupy solution. This solution contained 36% solids. The solution was clear and soluble when it was mixed with a 3% by weight sodium chloride solution. The tanning agent did not precipitate from solution on neutralization at pHs of from about 0 to about 7. The synthetic tanning agent was analyzed by the De Jong method and found to contain 1.1 free methylol groups per mole of sulfone employed.

**EXAMPLE V**

An alternate procedure for producing a shrunk grain synthetic tanning agent. 204 g. of dihydroxy diphenyl sulfone paste prepared by the procedure described in part (A) of Example I above was charged into a reaction vessel. The paste contained 78% by weight of solids, the solids being 98% by weight of a mixture of pure sulfone isomers and 2% by weight of impurities. The mixture of sulfone isomers weighed 156 g. (0.625 mole). The sulfone isomers in the mixture were present in a weight ratio of 88% of the 4,4'-dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-dihydroxy diphenyl sulfone isomer. The 2% by weight of impurities in the mixture consisted of polymeric sulfones, phenol sulfonic acids, other byproducts and the like. 400 g. of water, 250 g. of 2-naphthalene sulfonic acid mixture (about 75% by weight active) which contained 0.71 mole of 2-naphthalene sulfonic acid and was prepared by the procedure described in Example II above and 101 g. (1.25 mole) of formaldehyde solution (37% by weight active) were then charged into the reaction vessel and were mixed at room temperature. The molar ratio of formaldehyde to dihydroxy diphenyl sulfone isomers in the mixture was two moles of formaldehyde per mole of dihydroxy diphenyl sulfone. The reaction mixture was heated to the reflux point, that is, about 102°C and became a clear solution immediately. The reaction mixture was refluxed at 102°C for 15 hours, cooled to room temperature and neutralized with cooling by the addition of 106.5 g. of 50% by weight sodium hydroxide solution and 50 g. of water. The product of the reaction was about 1100 g. of a clear syrupy liquid containing 35% solids by weight. The clear syrupy liquid was the desired synthetic tanning agent. The properties of the synthetic tanning agent were comparable to those of the agent obtained in Example III above. That is, the tanning agent was soluble in salt solutions containing at least 2.5% by weight of sodium chloride and the agent did not precipitate from solution on neutralization at pHs from about 0 to about 7. Analysis of the synthetic tanning agent by the De Jong method showed that it contained 1.0 free methylol groups per mole of sulfone employed.

**EXAMPLE VI**

A synthetic tanning agent was prepared according to the procedure described in Example I of U.S. Patent No. 3,010,779, was synthesized and evaluated in the following manner.

255 g. of a dry 98% by weight pure crystalline dihydroxy diphenyl sulfone isomers mixture prepared by the procedure given in part (A) of Example I above, 150 g. of water and 35 g. of 45% by weight sodium hydroxide solution were charged into a reaction vessel and mixed. The sulfone isomer mixture contained 98% by weight of sulfone isomers and 2% by weight of impurities. The mixture of sulfone isomers weighed 250 g. (1.0 mole). The sulfone isomers in the mixture were present in a weight ratio of 88% of the 4,4'-dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-dihydroxy diphenyl sulfone isomer. The 2% by weight of impurities in the mixture consisted of polymeric sulfones, phenol sulfonic acids and the like. 87.5 g. (0.88 mole) of formaldehyde solution (37% by weight active) was then charged into the reaction vessel and the resulting reaction mixture was heated at its boiling point for 3 hours to obtain a condensation product. The resulting condensation product was then mixed with 275 g. (1.12 mole) by weight of the naphthalene sulfonic acid obtained by the procedure described in U.S. Patent No. 1,972,754 and the mixture was reacted by heating at 120°C for 1.5 hours. When an attempt was made to neutralize the reaction product of this mixture with 50% sodium hydroxide solution, the synthetic tanning agent precipitated. Analysis of the synthetic tanning agent by the De Jong method showed that it contained 0.9 free methylol groups per mole of sulfone employed.

This example demonstrated that synthetic tanning agent prepared in accordance with this procedure could not be satisfactorily neutralized to a pH in range of about 0 to about 7 so that the free sulfonic acid was completely neutralized and the naphthalene sulfonic acid was partially neutralized. During the neutralization when only a fraction of the free sulfonic acid was neutralized, precipitation of the tanning agent began and became increasingly heavy as the pH was raised gradually above 6. Further, the agent was not soluble in a salt solution containing 0.1% by weight of sodium chloride.

**EXAMPLE VII**

This example demonstrates the preparation of a synthetic tanning agent from a crude and impure dihydroxy diphenyl sulfone. 162 g. (1.72 mole) of phenol, 87 g. (0.85 mole) of sulfonic acid (96% by weight active) and 50 g. of monochlorobenzene were mixed together in a reaction vessel and heated to a maximum temperature of about 168°C. The water formed during reaction was removed by azeotropic distillation. After the dihydroxy diphenyl sulfone was formed, the reaction mixture was neutralized with a solution containing 110 g. of 50% by weight sodium hydroxide solution and 300 g. of water. Monochlorobenzene remaining in the reaction mixture was removed by azeotropic distillation. After all of the monochlorobenzene had been removed, the reaction mixture was cooled to 20°C and a suspension of white crystals in a pink mother liquor was obtained. The suspension of crystals in mother liquor was then used directly without purification. The clear syrupy liquid was the desired synthetic tanning agent. The properties of the synthetic tanning agent were comparable to those of the agent obtained in Example III above. That is, the tanning agent was soluble in salt solutions containing at least 2.5% by weight of sodium chloride and the agent did not precipitate from solution on neutralization at pHs from about 0 to about 7. Analysis of the synthetic tanning agent by the De Jong method showed that it contained 1.0 free methylol groups per mole of sulfone employed.

100 g. (1.23 mole) of formaldehyde (37% by weight active) was added to the suspension of the crystals in the mother liquor and the resulting mixture stirred for 1 hour and 25 minutes at 24°C. The reaction temperature was then gradually raised to 55°C. The mixture was then reacted at 50°C to 55°C for 24 hours. The formaldehyde content of the reaction mixture was determined by the procedure described in Example III above and found to be 1.02% by weight. The reaction mixture was then reacted at 50°C to 52°C for 17 additional hours. The formaldehyde content was found to be 0.0% by weight. The mixture was then cooled to room temperature and 70 g. of sulfonic acid (96% by weight active) and 70 g. of water were added. The reaction product was a suspension of solids in salt water. The solids were allowed to settle and the salt water removed by decantation. The solids were then washed three times with 500 g. quantities of water cooled to 10°C. After the third wash, the formaldehyde content of the third wash water was determined and found to be 0.0% by weight. After the methylolated
crude sulfone mixture was washed free of formaldehyde, it was analyzed by the De Jong method and found to contain 1.8 free methylol groups per mole of sulfone.

230 g. of 2-naphthalene sulfonic acid mixture, which contained 0.5 mole of sodium sulfide, was added to the mixture and re-fluxed at 110° C. for 5 hours. The reaction mixture was then cooled to 30° C. and 375 g. of water and 95 g. of 50% by weight sodium hydroxide solution were added. The resulting product was a clear solution of a synthetic tanning agent containing 44% by weight solids and had a pH of 2.2 as is. Analysis of the tanning agent by the De Jong method showed that it contained 0.4 methylol groups per mole of sulfone employed instead of the expected 0.7 methylol groups per mole of sulfone. The unaccounted free methylol groups had reacted with the byproducts present in the crude sulfone mixture. Such byproducts included polymeric sulfones, phenolic sulfonic acids and the like. The agent precipitated from 2% by weight sodium chloride solution.

**EXAMPLE VIII**

This example demonstrates the preparation of a synthetic tanning agent from a dihydroxy dimethyl diphenyl sulfone prepared from ortho cresol.

A dihydroxy diphenyl sulfone was prepared from ortho cresol by using the procedure given in Example I (A) above and substituting an equal molar quantity of ortho cresol for phenol. The resulting dihydroxy dimethyl diphenyl sulfone was washed, filtered and dried. 139 g. (0.5 mole) of the dihydroxy dimethyl diphenyl sulfone obtained from this preparation was mixed with 400 cc. of water, 81 g. (1 mole) of formaldehyde solution (37% by weight) and 300 g. (0.86 mole) of 2-naphthalene sulfonic acid solution (75% by weight active) prepared according to the procedure in Example II above. The resulting reaction mixture was re-fluxed at 102° C. for 10 hours in a reaction vessel, cooled to 20° C. and neutralized to a pH of 2.8 by the addition of 171 g. of 50% by weight sodium hydroxide solution. The mixture was cooled at 20°-40° C. during neutralization. The neutralized product was a synthetic tanning agent in the form of a clear solution containing 38.4% by weight of the synthetic tanning agent. The product was analyzed by the De Jong method and found to contain 0.3 free methylol groups per mole of sulfone employed.

**EXAMPLE IX**

Evaluation of the synthetic tanning agents prepared in Examples III through VIII.

300 g. of drained pickled stock gauging 5 oz. and having a pH of 2.0 was floated in 300 cc. of a 4% by weight salt solution for 30 minutes to rewet and soften the stock. The solution was drained. 150 g. of water and 90 g. of the synthetic tanning agent obtained in Example III above was added. The stock was rotated for 4 hours in the synthetic tanning agent and water solution. After 4 hours of rotation, exhaust of the synthetic tanning agent was complete. Exhaust was determined by the Official A.I.C.A. Method A-25. The exhausted solution was drained and a new float of 300 cc. of water and 24 g. of a chrome liquor containing 25% chromium oxide of 33% basicity were added. The sample of stock was rotated in this liquor for 12 hours. Then 30 cc. of a 10% by weight sodium bicarbonate solution was added and the sample was rotated for an additional two hours. The sample was taken out of the drum, horseted for 48 hours, then washed in fresh water, dyed and fat liquored in the usual manner. After fat liquoring, the sample was taken out of the drum, dried, staked and toggled on the wet frame. After drying, the leather sample was finished in the usual manner. The leather sample produced by this procedure had a round feel and was soft and strong. The pattern developed on the grain of the leather by the above tanning procedure was carefully examined. The pattern was found to be highly uniform, spread evenly over all of the surface of the leather with high depth. No coarseness whatsoever in the pattern was noted and the pattern gave an overall picture of a natural, uniform, fine pattern. On stretching of the leather sample, the sample immediately recovered the same pattern after the stretch was released.

The same test procedure was used to evaluate samples of the synthetic tanning agents obtained in Examples IV through VIII. The following results were obtained. Stock tanned with the products of Examples IV and V by this procedure showed the same favorable results as obtained with the product of Example III. The leather obtained with Example IV was superior to that obtained with the product of Example III and the properties of the leather obtained with the product of Example V were closest in quality and properties to that obtained with the product of Example IV. Leather tanned with the product of Example VI showed a very poor and non-uniform shrinking pattern having low depth, poor surface coverage by the pattern and was inferior in feel and strength. The leather obtained with the product of Example VII was slightly better in appearance to that obtained with the product of Example VI but was very inferior to the leather obtained with the product of Example III, IV and V. Leather obtained with the product of Example VIII had a very poor non-uniform pattern. When the sample of leather obtained with the product of Example VI was neutralized to a pH of 2.2 as is and the precipitated mixture was used in the evaluation on leather, equally poor results were obtained as with the unneutralized product. It was noted that the precipitated tanning agent dissolved gradually during the tanning procedure but that the gradual solution of the precipitated tanning agent did not improve the shrunken grain leather pattern. As pointed out above, the grain must be shrunken during the initial phase of the tanning process.

**EXAMPLE X**

Shaved chrome tanned stock was partly dechromed with 5% by weight oxalic acid solution, washed thoroughly and then retained in a 50% float by the procedure described in Example IX above with 30% by weight of each of the synthetic tanning agents described in Examples III through VIII above. When the samples of finished shrunken grain leather were examined, the same results as those obtained in Example IX above were noted and the only distinction was that the differences between the various tanning agents were more pronounced. This meant that the synthetic tanning agents produced in Examples IV and V were superior to all of the others. The leather obtained with the synthetic tanning agent of Example III was good and of excellent quality. Leather obtained from Example VI was extremely poor. Leather obtained with the synthetic tanning agents of Examples VII and VIII were also extremely poor.

**EXAMPLE XI**

500 g. of shaved chrome calf leather was dechromed with an oxalic acid solution containing 25 g. oxalic acid in 500 g. of water. When the shrinkage temperature of the stock dropped from an original value of 212° F. to 110° F., the dechromed leather was washed thoroughly and then treated in a tanning liquor containing 250 g. of water with 150 g. of the synthetic tanning agent of Example IV. The leather samples were rotated in this liquid for 5 hours. The tanning liquor was drained, the samples refloated with 500 g. water and 40 g. of a chrome liquor containing 25% chromium oxide of 33% basicity were added. After 8 hours of rotation on frames. After washing, the leather sample was finished in the usual manner. The leather sample produced by this procedure had a round feel and was soft and strong. The pattern developed on the grain of the leather by the above tanning procedure was carefully examined. The pattern was found to be highly uniform, spread evenly over all of the surface of the leather with high depth. No coarseness whatsoever in the pattern was noted and the pattern gave an overall picture of a natural, uniform, fine pattern. On stretching of the leather sample, the sample immediately recovered the same pattern after the stretch was released. The same test procedure was used to evaluate samples of the synthetic tanning agents obtained in Examples IV through VIII. The following results were obtained. Stock tanned with the products of Examples IV and V by this procedure showed the same favorable results as obtained with the product of Example III. The leather obtained with Example IV was superior to that obtained with the product of Example III and the properties of the leather obtained with the product of Example V were closest in quality and properties to that obtained with the product of Example IV. Leather tanned with the product of Example VI showed a very poor and non-uniform shrinking pattern having low depth, poor surface coverage by the pattern and was inferior in feel and strength. The leather obtained with the product of Example VII was slightly better in appearance to that obtained with the product of Example VI but was very inferior to the leather obtained with the product of Example III, IV and V. Leather obtained with the product of Example VIII had a very poor non-uniform pattern. When the sample of leather obtained with the product of Example VI was neutralized to a pH of 2.2 as is and the precipitated mixture was used in the evaluation on leather, equally poor results were obtained as with the unneutralized product. It was noted that the precipitated tanning agent dissolved gradually during the tanning procedure but that the gradual solution of the precipitated tanning agent did not improve the shrunken grain leather pattern. As pointed out above, the grain must be shrunken during the initial phase of the tanning process.
skin. The same procedure was repeated with the synthetic
tanning agent of Example V with equally good results.

**EXAMPLE XII**

100 lbs. of pickled cowhides were floated in 200 lbs. of
a 4% by weight salt solution for one hour to soften the
stock. The salt solution was drained and 50 lbs. of water
and 10 lbs. of the synthetic tanning agent produced ac-
cording to Example V above were added as a tanning
liquor. The hides were rotated for six hours until the
exhaust of the synthetic tanning agent was complete. Sub-
sequently, the tanning liquid was drained and the hides
refloated in 100 lbs. water, 9 lbs. of a chrome liquor con-
taining 25% by weight chromium oxide of 40% basicity
was added. The hides were rotated in this liquor for 12
hours. Then 0.8 lbs. of sodium bicarbonate dissolved in
8 lbs. water was added over a period of one-half hour and
the hides rotated for an additional 2 hours. The hides
were taken out from the drum, hosed for 48 hours, then
washed in water, neutralized with sodium bicarbonate
solution, dyed and fat-liquored in the usual way. After
this procedure was finished, the hides were taken out,
dried, stacked and tacked on frames. After drying, they
were finished in the usual way. The appearance of the
shrunken grain leather produced by this procedure was
examined. The leather had a round feel and was soft and
strong. The shrunken grain pattern on the leather was
examined and found to show a uniform picture with no
difference in the pattern formed on the middle parts, neck
parts, tail parts or flanks of the hides. The pattern was
deep, very uniform, fine and natural looking. Even the
most powerful stretching of the hides did not make the
pattern disappear and recovery of the pattern after release
of the stretch was complete.

**EXAMPLE XIII**

10 lbs. of shaved chrome tanned side leather were par-
tially dechromed by treatment with a 5% by weight oxalic
acid solution. The partially dechromed hides were washed
thoroughly and the wash water was drained. 5 lbs. of
water and 3 lbs. of the synthetic tanning agent of Example
IV above were added as a tanning liquor and the hides
were rotated in this liquor for 5 hours. The tanning liquor
was drained and a float of 10 lbs. of water and 3 lbs. of
a chrome liquor containing 25% chromium oxide of 33% basicity
was added. The hides were rotated in this liquor for 2 hours. Then 0.12 lbs. of sodium bicarbonate dis-
solved in 1.2 lbs. water was added and the hides rotated
for two additional hours. The float was drained and 10
lbs. water, and 1 lb. of a 35% quebracho extract were added.
The hides were rotated for five additional hours, then
washed and finished in the usual way. The finished
shrunken grain leather was examined and showed very
high depths of the pattern form distributed uniformly over
the entire area of the hides. The feel of the leather was
round. The shrunken grain pattern on the leather recover-
ced completely after release of stretching. The finished
leather was soft and strong.

**EXAMPLE XIV**

This example demonstrates the preparation of a
shrunken grain synthetic tanning agent using 95% by
weight dihydroxy diphenyl sulfone isomer mixture.

(A) Preparation of 95% by weight pure dihydroxy diphenyl
diphenyl sulfone isomer mixture.

1148 g. (12.2 moles) of phenol, 612 g. (6 moles) of sulfuric
acid (96% by weight active) and 125 g. mono-
chlorobenzene were charged into a reaction vessel
equipped with an agitator and a water separation trap.
The reaction mixture was heated to the reflux tempera-
ture which was about 140° C. The escaping vapors of chloro-
benzene and water formed during the reaction were con-
densed in the condenser and were separated in the water
trap. The dry chlorobenzene was returned to the reaction
mixture. Reaction temperature was gradually increased to
a temperature between 165° C. and 170° C. After from
about 210 cc. to 215 cc. of water had been separated by
azeotropic distillation, the reaction mixture was titrated
to determine its acidity. A 10 g. sample of the reaction
mixture at this point should not require more than 19.00
cc. to 20.00 cc. of 0.5 N sodium hydroxide solution to
neutralize the sample to a pH of 7.0.

After the desired acidity was obtained, 500 cc. of water
was added carefully to the reaction product. The reaction
product was then neutralized to a pH between 5 and 6
by the cautious addition of from about 120 g. to about
130 g. of 50% by weight sodium hydroxide solution. Ap-
proximately 1,000 cc. of water was then added to the reac-
tion product and the resulting mixture was azeotropically
distilled to remove the chlorobenzene. After all of the
chlorobenzene was stripped from the reaction mixture,
an additional 1,000 cc. of water was added and the result-

ing solution of the reaction product was heated to its
boiling point. A clear solution was obtained at the boil-
ing point. The clear solution was then transferred to a
reaction vessel containing approximately 4,000 cc. of boil-
ing water and the resulting dihydric alcohol was allowed
to cool slowly to room temperature with vigorous agita-
tion. Dihydric diphenyl sulfone precipitated in the form
of cream colored crystals from the solution during cooling.

The precipitated crystals were filtered off on a filter press
without washing and dried at 105° C. The dry product
was analyzed for its actual sulfone content and found
to contain 95% by weight of pure dihydroxy sulfone
isomers and 5% by weight of impurities. The iso-
mers in the mixture consisted of 4,4'-dihydric diphenyl sulfone
and 4,2'-dihydric diphenyl sulfone. The 5% by
weight of impurities in the mixture included polymeric
sulfones, phenol sulfonic acids, other by-products and the
like.

(B) Preparation of a shrunken grain synthetic tanning agent
by using a 95% by weight pure dihydroxy diphenyl sulfone
isomer mixture.

164.5 g. of the 95% by weight pure sulfone isomer mix-
ture obtained in part (A) and containing 156 g. (0.625
mole) of dihydroxy diphenyl sulfone isomers, 426 g. of
water, 248 g. of 2-naphthalene sulfonic acid solution con-
taining 0.653 mole of sulfonic acid, 0.394 mole of sul-
furic acid and the balance being water, and 101 g. aque-
ous formaldehyde solution containing 1.25 mole of for-
maldehyde were mixed together and heated to reflux.
The molar ratio of formaldehyde to sulfone was 2 moles of
formaldehyde to 1 mole of sulfone. The reflux tempera-
ture of the mixture was 101° C. The refluxing solution
was slightly hazy in appearance. After 15.5 hours of re-
flux, the reaction mixture was cooled to 40° C. and neu-
tralized with 106 g. of 50% by weight sodium hydroxide
solution and 50 g. of water. No precipitate formed during
the neutralization but the solution had a faint haze. 10 g.
of filter aid was added and the solution was filtered through
a Knier pressure filter. It was then brilliantly clear.

Analysis of the shrunken grain synthetic tanning agent
showed that it contained 0.9 mole of free methylol groups
der than 1 mole of sulfone employed in the reaction. The prop-
erties of the tanning agent were comparable to the syn-
thetic tanning agent of Example V above.

**EXAMPLE XV**

This example demonstrates preparation of a
shrunken grain synthetic tanning agent by using a 100% by weight pure dihydroxy diphenyl sulfone isomer mixture.

The procedure given in Example IV above was re-
peated with the exception that 117.5 g. (0.47 mole) of
100% by weight of a pure crystalline dihydroxy diphenyl sulfone isomer mixture prepared by the procedure given in part (B) of Example I above was employed instead of
154 g. of sulfone paste. The sulfone isomers in the mix-
ture were present in a weight ratio of 88% of the 4,4'-
dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-
dihydroxy diphenyl sulfone isomer. The properties of the
synthetic tanning agent were comparable to those of the synthetic tanning agent produced in Example IV. The foregoing examples demonstrate that the synthetic tanning agents of the present invention produce shrunken grain leathers having deep uniform patterns which completely recover after stretching and release of the stretch. The examples given below, that is, Examples XVI through XVIII further demonstrate that synthetic tanning agent solutions prepared by procedures outside the scope of the invention do not produce shrunken leathers having satisfactory properties.

EXAMPLE XVI

This example is directed to preparing a tanning agent from an impure, crude sulfone.

200 g. of a crude dihydroxy diphenyl sulfone isomer mixture was prepared according to the procedure given in Example VII above, the only difference being that the reaction was carried half way to completion. The crude sulfone contained 80% by weight solids, was about 40% pure by weight and contained 80 g. (0.32 mole) of dihydroxy diphenyl sulfone isomers. The 60% by weight impurities in the mixture included polymeric sulfones, phenol sulfonic acid, other byproducts and the like. This quantity of sulfone represented a 37% yield instead of the expected 75% yield. The crude sulfone was mixed with 100 g. of water and 95 g. (1.17 mole) of aqueous formaldehyde solution (37% by weight active). The mixture of formaldehyde to sulfone was 3.66 moles of formaldehyde to 1 mole of dihydroxy diphenyl sulfone. The mixture was heated to 50°C and held at 50°C with agitation for 12 hours. After heating 12 hours at 50°C, a gummy precipitate formed from the solution. The water layer was decanted from the gummy resinous precipitate and the precipitate washed three times with 500 cc. quantities of cold water. Analysis showed that the third 500 cc. water wash was free of formaldehyde, that is, the precipitate did not contain any free or unreacted formaldehyde. The crude methylolated sulfone mixture contained 1.4 free methylol groups per mole of sulfone employed. 125 g. (0.33 mole) of naphthalene sulfonic acid mixture (about 75% by weight active) prepared by the procedure described in Example II above was added to the washed resinous precipitate and then 50 g. of water was added. The resulting mixture was heated to reflux and refluxed for 2 hours. No solubilization of the reactants occurred during the 2 hours that the reactants were refluxed. Further, no appreciable solubilization of the reactants occurred even prolonged refluxing of the reaction mixture. After cooling the reaction mixture, the major portion of the reaction product formed a gummy resinous mass, which was insoluble in water. Neutralization of the reaction product to a pH of 3.5 by the addition of sodium hydroxide solution did not solubilize the resinous reaction product. Further, the reaction product was not soluble in a salt solution containing 0.1% by weight sodium chloride. The resinous product contained 0.0 free methylol groups per mole of sulfone employed. The product was not in suitable form for use as a synthetic tanning agent in producing shrunken grain leather.

This example demonstrated the use of a crude dihydroxy diphenyl sulfone mixture which had a purity of about 40% by weight and was outside the purity limit of this invention did not give a satisfactory shrunken grain tanning agent even through the quantities used, that is, one mole of the dihydroxy diphenyl sulfone mixture, 2.67 moles of formaldehyde and 1.33 moles of 2-naphthalene sulfonic acid, were within the limits of this invention.

EXAMPLE XVII

This example is directed to the preparation of a tanning agent from a crude sulfone.

(A) 188 g. (2 mole) phenol, 102 g. (1 mole) sulfuric acid 98% by weight and 25 cc. chlorobenzene were heated to reflux and the water formed during the reaction was removed azeotropically. After refluxing the reaction mixture for 75 minutes, the reflux temperature was 175°C, and a total of 37 cc. of water had been removed by azeotropic distillation. The reaction mixture was neutralized with 13.5 g. of sodium hydroxide and 94 g. of water. The neutralized crude sulfone dissolved when the mixture was heated to boiling point. 200 g. of water was added to the crude dihydroxy diphenyl sulfone. The crude sulfone isomer mixture was 75% pure by weight. The 25% by weight of impurities in the mixture included polymeric sulfones, phenol sulfonic acids, other byproducts and the like.

(B) 128 g. (1 mole) naphthalene was reacted with 160 g. (1.6 mole) sulfuric acid (98% by weight) for 1 hour at 155°C. The reaction mixture was cooled to 90°C and 100 g. of ice was added to the reaction mixture at room temperature. The reaction mixture was a mixture containing about 75% by weight of 2-naphthalene sulfonic acid plus excess sulfuric acid, that is, 1.0 mole of 2-naphthalene sulfonic acid and 0.6 mole of sulfuric acid.

(C) The crude dihydroxy diphenyl sulfone mixture, which represented 0.75 mole of 100% by weight pure dihydroxy diphenyl sulfone isomers obtained in part (A) above was mixed with the solution of 2-naphthalene sulfonic acid (1.0 mole) obtained in part (B) above and 296 g. of water added. A total of 162 g. (2 moles) of aqueous formaldehyde solution (37% by weight active) was added and the resulting reaction mixture heated to reflux. The reaction mixture contained 0.75 mole of sulfone and 2.00 moles of formaldehyde and had a molar ratio of formaldehyde to sulfone of 2.67. The reactants in the reaction mixture did not dissolve in the reaction mixture but remained insoluble even after the reaction mixture had been refluxed for 14 hours. When the reaction mixture was cooled and neutralized, a gummy precipitate was obtained. The reaction product was insoluble over the entire neutralization range, that is, from a pH of about 0 to about 7. Further, the final product was insoluble in salt solutions containing as little as 0.1% by weight sodium chloride. The final reaction product contained 0.00 methylol groups per mole of sulfone employed. This product was not in suitable form for use as a synthetic tanning agent in producing shrunken grain leather.

This example demonstrated that use of a crude dihydroxy diphenyl sulfone isomer mixture which had a purity of 75% by weight and was outside the purity limits of this invention did not give a satisfactory shrunken grain synthetic tanning agent even though the quantities used, that is, one mole of the dihydroxy diphenyl sulfone mixture, 2.67 moles of formaldehyde and 1.33 moles of 2-naphthalene sulfonic acid, were within the limits of the present invention.

EXAMPLE XVIII

This example is directed to preparing a tanning agent with a molar quantity of formaldehyde outside the limits of the present invention.

127.5 g. of a dry, crystalline dihydroxy diphenyl sulfone isomer mixture of 98% purity by weight as described in Example I(A) above, 140 g. (0.5 mole) of 2-naphthalene sulfonic acid mixture as described below, 500 g. of water and 55 g. (0.68 mole) of aqueous formaldehyde solution (37% by weight active) were mixed and heated to reflux. The mixture of sulfone isomers weighed 125 g. (0.5 mole). The sulfone isomers in the mixture were present in a weight ratio of 88% of the 4,4'-dihydroxy diphenyl sulfone isomer to 12% of the 4,2'-dihydroxy diphenyl sulfone isomer. The 2% by weight of impurities included polymeric sulfones, phenol sulfonic acids, other byproducts and the like. The naphthalene sulfonic acid was prepared by the procedure given in Example XVII (B) above with the exception that the sulfuric acid was not added and the sulfonic acid was substantially anhydrous. After 18 hours at reflux, the mixture was neutralized with 86 g. of 50% by weight sodium hydroxide solu-
tion and 100 g. of water to obtain a synthetic tanning agent solution having a pH of 2.5. The solution contained 30% by weight solids. The molar ratio of formaldehyde to sulfone was 1.35:1 and the synthetic tanning agent contained 0.36 free methylol groups per mole of sulfone employed, that is, the tanning agent contained about 0.4 methylol groups per mole of sulfone employed. The tanning agent was evaluated as a shrunken grain tanning agent for leather. The agent did not produce satisfactory shrinking effects, that is, there were few scattered patterns on the leather and none of the patterns had depth.

This example demonstrated that use of less than 1.5 moles of formaldehyde per mole of sulfone did not give a satisfactory shrunken grain tanning agent because the agent contained less than 0.5 methylol groups per mole of sulfone employed and was outside the limits of the present invention.

What is claimed is:

1. A water soluble shrunken grain synthetic tanning agent in substantially monomeric form comprising the reaction product of

(a) one mole of a sulfone having a purity of from about 95% to 100% by weight selected from the group consisting of 4,4'-dihydroxy diphenyl sulfone, 2,2'-dihydroxy diphenyl sulfone and mixtures thereof,

(b) from about 1.5 moles to about 5.0 moles of formaldehyde per mole of said sulfone, and

(c) from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of said sulfone, said (a), (b) and (c) being mixed at about room temperature, and thereafter reacted at temperatures of from about 20° C. to about 150° C. in aqueous solution until a clear solution is obtained with the proviso that pressure is employed at temperatures between about 110° C. and about 150° C., and water being present in an amount of from about three to about five times the weight of said sulfone, and with the further proviso that said reaction product contains at least 0.5 free methylol groups per mole of said sulfone, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7.

2. The shrunken grain synthetic tanning agent as described in claim 1 wherein said sulfone has a purity of about 95% to 100% by weight selected from the group consisting of methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 2,2'-dihydroxy diphenyl sulfone, methylolated 2,2'-dihydroxy diphenyl sulfone and mixtures thereof wherein said sulfone contains from about 1.5 to about 4.0 free methylol groups per mole of said sulfone, said methylolated sulfone being prepared by reacting about one mole of a disodium salt of dihydroxy diphenyl sulfone having a purity of from about 95% to 100% by weight selected from the group consisting of methylolated 4,4'-dihydroxy diphenyl sulfone, the disodium salt of 4,4'-dihydroxy diphenyl sulfone, the disodium salt of 2,2'-dihydroxy diphenyl sulfone, and mixtures thereof and from about 1.5 moles to about 5.0 moles of formaldehyde at about 20° C. to about 55° C. in water present in an amount of from about one and one-half to about two times the weight of said diphenyl sulfone and at a pH of about 9.5 to about 10, thereby forming the disodium salt of said methylolated sulfone and thereafter precipitating said methylolated sulfone by acidification of said disodium salt of said methylolated sulfone and

3. A water soluble shrunken grain synthetic tanning agent in substantially monomeric form comprising the reaction product of

(a) one mole of a methylolated sulfone having a purity of from about 95% to 100% by weight selected from the group consisting of methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 2,2'-dihydroxy diphenyl sulfone, and mixtures thereof selected from the

(b) from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of said sulfone, said (a) and (b) being mixed at about room temperature, and thereafter reacted at temperatures of from about 50° C. to about 150° C. in aqueous solution until a clear solution is obtained with the proviso that pressure is employed at temperatures between about 110° C. and about 150° C., and water being present in an amount of from about one-half to about two times the weight of said sulfone, and with the further proviso that said reaction product contains at least 0.5 free methylol groups per mole of said sulfone, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7.

4. The shrunken grain synthetic tanning agent as described in claim 3 wherein said agent is the reaction product of

(a) one mole of said methylolated sulfone containing from about 2.0 to about 2.5 free methylol groups per mole of sulfone and having a purity of from about 95% to 100% by weight, and

(b) from about 0.9 mole to about 1.2 moles of 2-naphthalene sulfonic acid per mole of said sulfone.

5. The shrunken synthetic tanning agent as described in claim 3 wherein said sulfone has a purity of about 98% by weight.

6. A process of preparing a water soluble shrunken grain synthetic tanning agent in substantially monomeric form which comprises mixing together at about room temperature and thereafter reacting together at from about 20° C. to about 150° C. in aqueous solution until a clear solution is obtained, a reaction mixture comprising

(a) one mole of a sulfone having a purity of from about 95% to 100% by weight selected from the group consisting of 4,4'-dihydroxy diphenyl sulfone, 4,4'-dihydroxy diphenyl sulfone, and 2,2'-dihydroxy diphenyl sulfone and mixtures thereof,

(b) from about 1.5 moles to about 5.0 moles of formaldehyde per mole of said sulfone, and

(c) from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of said sulfone, with the proviso that pressure is employed at temperatures between about 110° C. and about 150° C., and water being present in an amount of from about three to about five times the weight of said sulfone, and with the further proviso that said reaction product contains at least 0.5 free methylol groups per mole of said sulfone, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7.

7. The process as described in claim 6 wherein said sulfone has a purity of about 98% by weight.

8. A process of preparing a water soluble shrunken grain synthetic tanning agent in substantially monomeric form which comprises mixing together at about room temperature, and thereafter reacting together at a temperature range of from about 50° C. to about 150° C. in aqueous solution until a clear solution is obtained, a reaction mixture comprising

(a) one mole of a methylolated sulfone having a purity of from about 95% to 100% by weight selected from the group consisting of methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 4,4'-dihydroxy diphenyl sulfone, methylolated 2,2'-dihydroxy diphenyl sulfone, and mixtures thereof selected from the

(b) from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of said sulfone, said methylolated sulfone being prepared by reacting about one mole of a disodium salt of dihydroxy diphenyl sulfone at about 20° C. to about 55° C. in water present in an amount of from about one and one-half to about two times the weight of said diphenyl sulfone and at a pH of about 9.5 to about 10, thereby forming the disodium salt of said methylolated sulfone and thereafter precipitating said methylolated sulfone by acidification of said disodium salt of said methylolated sulfone and
group consisting of the disodium salt of 4,4'-dihydroxy diphenyl sulfone, the disodium salt of 4,2'-dihydroxy diphenyl sulfone, the disodium salt of 2,2'-dihydroxy diphenyl sulfone and mixtures thereof, and from about 1.5 moles to about 5 moles of formaldehyde at about 20°C to about 55°C, in water present in an amount of from about one and one-half to about two times the weight of said diphenyl sulfone and at a pH of about 9.5 to about 10, thereby forming the disodium salt of said methylolated sulfone and thereafter precipitating said methylolated sulfone by acidification of said disodium salt of said methylolated sulfone, and

(b) from about 0.5 mole to about 2.0 moles of 2-naphthalene sulfonic acid per mole of said sulfone, with the proviso that pressure is employed at temperatures between about 110°C and about 150°C, and water being present in an amount of from about one-half to about two times the weight of said sulfone, and with the further proviso that said reaction product contains at least 0.5 free methylol groups per mole of said sulfone, is soluble in salt solutions containing at least 2.5% by weight of sodium chloride and when in solution does not precipitate on neutralization at a pH of from about 0 to about 7.

9. A process of preparing a water soluble shrunken grain synthetic tanning agent as described in claim 8 wherein said agent is the reaction product of

(a) one mole of a methylolated sulfone containing from about 2.0 to about 2.5 free methylol groups per mole of sulfone, and
(b) from about 0.9 mole to about 1.2 moles of 2-naphthalene sulfonic acid per mole of said sulfone.

10. The process as described in claim 8 wherein said methylolated sulfone has a purity of about 98% by weight.

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