

UNITED STATES PATENT OFFICE

2,469,437

QUINONE-RESORCINOL TANNING AGENT
AND PROCESSJoseph S. Kirk, Newtown, Pa., assignor to E. I.
du Pont de Nemours & Company, Wilmington,
Del., a corporation of DelawareNo Drawing. Application April 23, 1946,
Serial No. 664,428

6 Claims. (Cl. 8—94.33)

1

This invention relates to the production of certain interpolymerization products of quinone with resorcinol and is further directed to tanning compositions containing them; to processes for preparing such compounds, to processes using them for tanning of skins, and to skins tanned therewith.

The conversion of skins into leather is accompanied by profound changes in their physical characteristics. They become opaque, and a distinct fibrous structure becomes apparent. The stiffness characteristic of dry rawhides disappears to a great extent and they become comparatively flexible. They assume a characteristic attractive appearance and soft "feel." Tanning also renders the product imputrescible. For useful tanning these changes must be relatively permanent, and the leather should be resistant to de-tanning by water, at least at ordinary temperatures.

The ancient and well-developed art of tanning customarily effects the conversion of skins into leather by the use of vegetable preparations that contain tannins. Vegetable tanning materials, such as quebracho extract, produce leather which is only moderately resistant to de-tanning by water and the leather is particularly unstable when the temperature of the water exceeds about 180° F.

Tanning processes employing metal compounds, such as chromium sulfate, are also known. Such processes are, however, subject to a number of disadvantages in operation, and the leather produced is characteristically colored. While processes using metal compounds have been accepted for certain uses, they are by no means equivalent to vegetable tannages, and vegetable tannages have continued to be used despite their slowness and other disadvantages because of the quality and characteristics of the leather produced.

Numerous synthetic tanning materials have been proposed, but most of these are markedly inferior to the vegetable or metal compound tanning agents mentioned. In some instances the leather produced with known synthetic tanning agents is not sufficiently resistant to de-tanning by water, and in other cases the leather lacks the necessary "fullness" and "plumpness." Therefore, these synthetic tanning materials of the prior art are customarily used in conjunction with a vegetable tanning material or a metal compound tanning agent, and they are useful principally because of properties apart from their tanning characteristics.

2

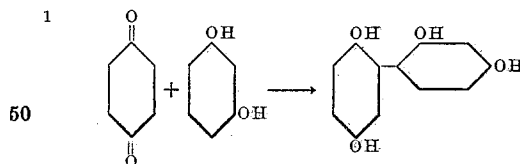
It is an object of this invention to provide novel chemical substances by the interpolymerization of quinone and resorcinol. It is a further object to provide processes for the production of such condensation products. It is a still further object to provide tanning compositions employing such condensation products either alone or in conjunction with known tanning materials to treat skins and hides to make leather. It is a further object of this invention to provide tanning processes which are rapid, simple to use, and easily controlled. It is a still further object to provide tanning processes by means of which there may be produced leather which is comparable with a vegetable tanned leather in quality and which has an even better resistance to shrinkage when treated with hot water and to de-tanning by aqueous solutions at ordinary temperatures. It is a still further object to produce a leather of improved solidity and characteristics and which is of increased stability. Still further objects will become apparent hereinafter.

The foregoing and other objects of this invention are attained by the preparation of an interpolymerization product of quinone, that is benzoquinone, with resorcinol, and by the use of such a condensation product in tanning compositions and tanning processes.

The tanning processes of the invention are particularly advantageous because the leather obtained is of excellent character. Leather produced is notable because of its solidity and its high shrinkage temperature which is indicative of greater stability of the tannage. The leather is stable at higher pH values than leather tanned with vegetable tanning agents.

Simple addition products of quinone and resorcinol can be prepared by two techniques which both yield well characterized, low molecular weight, crystalline products.

1. By mixing quinone and resorcinol in equimolecular proportions without a solvent, heating, and distilling, a condensation product was obtained which has the structure of a mono-resorcylic hydroquinone:

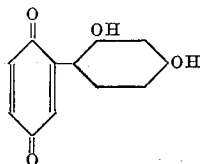


This product is highly soluble in water, and has no tanning action or precipitating action on proteins. By the use of oxidizing agents it can be

3

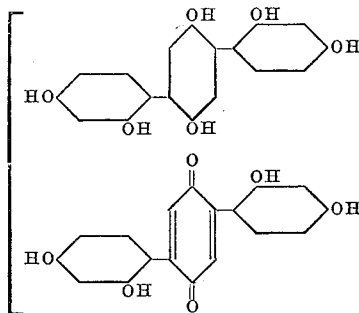
converted to mono-resorcylic quinone which is water-insoluble and therefore not adapted to use in tanning. The oxidized product has the formula:

2



2. By reacting quinone with an excess of resorcinol (molar ratio 1:5) at low temperature in 10% sulfuric acid, a crystalline precipitate is obtained which is diresorcylic quinhydrone; in other words, a complex comprising an equimolecular mixture of diresorcylic hydroquinone and diresorcylic quinone.

3



This crystalline complex is only slightly soluble in water and likewise has no tanning action on skins or precipitating action for proteins.

Now, the products of the present invention are polymers unlike the compounds obtained by any of the procedures outlined above. They may be prepared by a preferred process, as explained more fully hereinafter, by refluxing the reaction product of quinone and resorcinol in excess of about a half an hour.

The novel products of the invention are polymers of quinone and resorcinol. The polymers have more than four benzene rings and preferably more than ten benzene rings per molecule. Compounds more specifically preferred for use in tanning have from about twelve to eighteen benzene rings in the molecule. The products are further characterized by the fact that they contain an average of two oxygen-containing groups for each benzene ring.

The products of the invention are water-soluble, are amorphous, and are precipitated by acids. They are produced by processes under conditions which effect polymerization. The compounds of the invention are tanning agents while those water-soluble compounds shown at the right in formula 1 and in formulas 2 and 3 do not serve as tanning agents.

In referring to the products as polymers of quinone with resorcinol it will be understood that the polymerization probably proceeds by the quinone first reacting with resorcinol, and the condensation product thus formed reacts either with similar units or with further quantities of quinone and resorcinol. The polymers are characterized accordingly by containing recurring units of a benzene ring substituted with two oxygen atoms in a para relationship, derived from quinone, and a benzene ring substituted with two oxygen atoms in a meta relationship, derived from resorcinol.

With further reference to the structure of the polymer it will be understood that the recurring six-membered rings which contain two oxygen

4

atoms, as those in a para relationship derived from quinone, may be in a higher or lower state of oxidation as will be more particularly set out hereinafter. The oxygen may be present as a quinone-oxygen or as a hydroxy group. It is further to be observed that when comparatively larger proportions of quinone are used the polymer will be in a higher average state of oxidation.

Fortunately, the compounds of the present invention can easily be differentiated from the products as shown at the right in formula 1 and in 2 and 3, and one is easily able to select those polymerization conditions which produce compounds best adapted for use according to the present invention. Products of the present invention, then, are prepared by effecting polymerization of quinone and resorcinol, the conditions being sufficient to produce a product which will precipitate gelatin, but which is not polymerized to such an extent that it is insoluble.

The polymerization of quinone with resorcinol, according to the invention, may be carried out in any of the many ways generally well known to the art for effecting polymerization. The principal consideration in the ready selection of conditions for processes of the invention is to impose severe enough conditions that polymerization goes to a point such that the product is amorphous and will precipitate gelatin but not so severe as to result in the formation of an insoluble product. Those skilled in the art of effecting polymerization reactions will readily be able to suggest many specific procedures which will be suitable for preparing products of the invention.

The polymerization may suitably be effected, for instance, in an organic solvent such as acetone, methyl ethyl ketone, glacial acetic acid, ether-chloroform mixtures, acetone-chloroform mixtures, and cyclohexanone.

A catalyst such as a few drops of sulfuric acid or another acid such as acetic acid or hydrochloric acid is preferably included and, depending upon the other conditions selected, may be necessary to produce products of the invention.

The polymerization may also be effected in various of the ways known to the art, but polymerization must not be so severe as to produce insoluble resins.

If the polymerization is effected, as suggested above, in a suitable solvent, and with the use of a small amount of catalyst, the reaction may be permitted to proceed without the addition of heat until the exothermic reaction begins markedly to slow down. At this point heat is applied and the mixture refluxed for in excess of about, say, a half hour. The product of the invention is then separated from the reaction mixture by removal of the solvent.

The term "water soluble" is, standing alone, a little vague since many so-called insoluble materials are in fact soluble, at least to a certain extent. When the expression "water-soluble" is used herein it is intended to mean that the products are soluble in water to be usable as such in aqueous solutions and the solubility is, therefore, substantial. Generally it may be said that products can be designated water-soluble for the purpose of the present invention if, at 20° C., they are soluble to the extent of 10 grams per liter in water or slightly alkaline solutions of, say, pH 7.5.

The ratio of quinone to the resorcinol is an important consideration in the preparation of compositions of the invention. Materials of ratios from 0.6:1 to 4:1 have been prepared and used in tanning. For tanning compositions of wide

usefulness and variety of results there should be used a ratio of 1:1 to 3:1. It is to be observed that when such products are used as tanning agents they produce a leather having a shrink temperature above about 185° F. For tanning compositions of greatest stability, however, it is much preferred that the quinone:resorcinol ratio be from about 1.5:1 to 2.5:1. Below and above these ratios the shrink temperatures fall off very rapidly while within these ratios the shrink temperature is about 206° F. It will thus be seen that when the products are to be used as tanning agents for producing leather of very high shrink temperature, the narrower quinone:resorcinol ratio is critical.

As has been observed above, polymers of the invention may be in a higher or lower state of oxidation depending upon the precise conditions of preparation. An even greater variation in the state of oxidation of products produced as above may be effected by changing their state of oxidation by either treatment with an oxidizing agent or by treatment with a reducing agent.

A product of the invention may, for instance, be treated with such oxidizing agents as hydrogen peroxide, potassium permanganate, persulfates, air, or oxygen, or any other of the common oxidizing agents. Leather tanned using such oxidized products is of a somewhat dark color by reason of the oxidation.

Generally it is not preferred to oxidize agents of the invention for use in tanning. It will also be noted that in the usual tanning operation there is considerable aeration of the solution and there may accordingly be some oxidation during the tanning process, tho this will be much less than would be obtained if an effort were deliberately made to introduce air or oxygen. It will also be observed that instead of oxidizing the agents themselves before tanning, it is possible to oxidize the tanning solutions prior to or during tanning. Even after tanning is completed the finished leather may be treated with oxidizing agents tho this practice is not preferred.

Reducing of the agents of the invention may similarly be effected as by treatment with sodium bisulfite. As a matter of fact, it may even be found convenient to sell the products as bisulfite addition products. Leather prepared using an agent which has been treated with bisulfite has a lighter color than that produced without the use of reducing agents. Instead of using bisulfite, any other of the common reducing agents may be used, and there may be mentioned oxalic acid, stannous chloride, or nascent hydrogen produced as by the reaction of zinc dust with acetic acid in situ. Reduction may also be effected by catalytically reducing with hydrogen.

As with the oxidation, the reduction may be effected during the tanning or even may be applied to the tanned leather, tho such practices are not preferred.

Products of the invention are useful, as is more particularly set out hereinafter, for the treatment of skins to produce leather. They are also useful for many other purposes and they may be employed, for instance, as fungicides, bactericides and as contact insecticides, especially against aphids and red spiders. The compounds are bacteriostatic and this property may be found to enhance their usefulness for other purposes also.

In order that the invention may be better understood reference should be had to the following illustrative examples.

Example 1

A solution of quinone and resorcinol in acetone was made up with the following:

	Parts by weight
Quinone (2 mols) -----	216
Resorcinol (2 mols) -----	220
Acetone -----	800

The solution was heated to 50° C., and then heating was discontinued. There was then added 3 drops of sulfuric acid (50% H₂SO₄) as a catalyst. A vigorous reaction took place and the temperature rose to 70° C. The reaction was conducted under a reflux and in this period there was a considerable refluxing of the reaction mixture. The refluxing continued by reason of the heat of reaction for about fifteen minutes, then heat was applied as the refluxing slowed down, and the refluxing was continued until the total time of refluxing was one hour.

The solvent was removed by distillation under vacuum to a concentration of 85% solids, the temperature during distillation being maintained below about 70° C. The time required for concentration was one-half hour. The product obtained was heated in water to give a 50% solution (50% solids by weight), containing approximately 15% acetone. The vacuum used during distillation was 100 to 120 mm. of mercury.

The final solution obtained had a pH of 4.6. If desired, the acetone remaining in the product can be further removed tho care must be taken not to modify the product itself in this operation.

The amount of solvent used can be considerably varied and products have been made as in this example using from about 15 to 60 per cent of the reactants in the solvent. It is further to be noted that in a process such as that of this example the continuing of reflux beyond a total of about one-half hour appears to have but little effect upon the product. Reflux was continued up to about eight hours under the conditions shown and the product obtained was not substantially different from that described above.

The removal of acetone by distillation at atmospheric pressure, however, yields products which are only slightly soluble in water and it has been found necessary, as in this example, to remove acetone at reduced pressure below about 70° C., and preferably in a time not much in excess of about one-half hour. It will be understood that the distillation can be regarded as a part of the polymerization step and must be so conducted, as has previously been indicated, that the product finally obtained will be amorphous, will precipitate gelatin from solution but will still be water-soluble.

It is to be observed that when reference is made herein to the product precipitating gelatin from solution that the test is not particularly critical as to the manner in which it is conducted but it may be indicated that to determine whether a particular product will precipitate gelatin it is sufficient to make up a solution containing 1% by weight of gelatin and then add thereto one drop of a 10% aqueous solution of the product being tested at a temperature of 25° C.

A product was prepared as in Example 1 but using a quinone/resorcinol ratio of 2:1. The product was like that of Example 1 but was somewhat less soluble at the pH of the reaction.

The polymer as thus produced was examined to determine its character and its molecular weight. Successive portions of the product were precipitated from acetone by the use of increasing

amounts of chloroform. The individual fractions were vacuum dried, dissolved in methyl alcohol, and reduced under atmosphere of nitrogen using zinc dust and hydrochloric acid. The products thus obtained were precipitated by drowning in water, recovered by filtration, dried under nitrogen, acetylated with acetic anhydride in pyridine solution and the products thus obtained were dried. The products thus obtained for each of the fractions were then dissolved in benzene and their molecular weights determined by consideration of the lowering of the freezing point. The fractions, the per cent by weight which each represents of the original product, the molecular weight of the reduced and acetylated product, and the number of benzene rings in each fraction are tabulated below:

Fraction	Amount by Weight	Molecular Weight	Number of Benzene Rings per Molecule
	<i>Per cent</i>		
A.....	12	3,168	16
B.....	40	3,405	17.5
C.....	15.2	2,792	14
D.....	16.5	2,403	12
Filtrate-5% solids.....	16.3	307	1.6

A product prepared as in Example 1 was reduced using zinc dust and hydrochloric acid and the hydroxyl number determined. The results indicated that there is an average of about two hydroxyl groups for each benzene ring in the molecule.

The polymerization products of the invention are precipitated by acids, as has already been noted, and the pH at which precipitation occurs is related to the quinone/resorcinol ratio. In concentrations used for tanning, a product made using from about 3:1 to 4:1 of quinone/resorcinol precipitates at a pH around or a little below 7. Accordingly, in using such products in tanning it is desired to use slightly alkaline conditions and to maintain a pH of, say, about 7.5. As the ratio drops to 2.5:1 and on down to 2:1, the products become somewhat less easily precipitated and do not come out of solution until a pH of about 6.8 or so is reached. As the ratio goes still lower, a pH of about 5 effects precipitation of a product of 1.5:1 ratio while a pH of about 4 precipitates a product of about 1:1. Products of still lower ratio require somewhat lower pH values to effect precipitation.

The polymerization products above described may be used for the treatment of any type of skin adapted to be converted into leather or fur. It is to be observed that the term "skin" is used generically to include heavy skins such as cowhide, lighter skins such as goatskin and calfskin, and also skins of fur-bearing animals. It will naturally be necessary to adapt the processes to the type of skin to be treated. Those skilled in the art are well aware of such factors and may readily adapt the tanning agents of this invention to the needs of the particular tanning problem.

Skins to be tanned according to the processes of this invention may be prepared in any of the manners customary in the art, particularly for the preparation of skins for vegetable tanning. They may be unhaired, limed, delimed, and bated. The skins, if pickled, should be de-pickled before tanning, for, as will be mentioned hereinafter, it is preferred to effect tanning under substantially neutral conditions. The skins may be

given a salt-liquor treatment to soften them up and to render them of a more uniform condition as is the practice in the art.

While skins prepared in any manner may be treated according to the processes of this invention, it will ordinarily be desired that the skins be at a pH near 7, or slightly on the acid side. The tanning operation is conducted at about pH 6.5 to 7.5 and while the tanning solution may suitably be controlled to compensate for variance of the pH of skins, it will often be found advantageous to bring the skins to a suitable pH prior to introducing them into the tanning solution. Generally, it may be indicated that the tanning operation with the agents of the invention is conducted beginning at a pH of 6.5 to 7.5. The tanning is then finished off at a slightly lower pH ending up with a pH from about 5 to 7.

The products prepared as above will ordinarily be found to be slightly more acidic than is desired for a tanning bath and the pH may suitably be adjusted by the use of such alkalis as alkali metal hydroxides or carbonates, and ammonium hydroxide. When it is desired to lower the pH of the tanning solution there may be used any acidic material such as lactic, hydrochloric, sulfuric, acetic, phosphoric, sulfamic, and formic acids.

Tanning processes, according to the present invention, are closely related to the vegetable tanning processes heretofore used and the close kinship between the processes makes it unnecessary to enter into great detail regarding tanning technique since those skilled in the art may use the tanning agents of the present invention in accordance with the practices already common in the art for vegetable tanning.

While the agents of the present invention may be used alone for tanning with excellent results, they may, if desired, be used together with any other tanning agent or tanning assistant known to the art. Again, in accordance with practices already well known, they may be used prior to or following other tannages. They may be used, for instance, in conjunction with vegetable tanning materials such as quebracho extract, with chrome tans, with synthetic tanning agents containing sulfonic acid groups, or with formaldehyde. They may also be used in conjunction with the tanning agents shown in the Graves Patents 2,205,882 and 2,205,883.

The hides following treatment with a tannage of the present invention may be further treated with a soluble salt of aluminum, iron, titanium, copper, or chromium as in the Kirk Patent 2,205,901.

Leather produced according to the processes of this invention may be subjected to any of the various kinds of finishing treatments customarily used. The leather, if desired, may be suitably filled or given any of the numerous surface treatments customary in the art.

Example 2

Two hundred and twenty two parts by weight of a 25% aqueous solution of a quinone/resorcinol polymerization product prepared as in Example 1 was diluted with water to make a tanning bath totalling 1000 parts by weight and having a pH of 6.8. To this solution was added 462 parts by weight of limed and bated steer hide and the solution agitated mildly for a period of ten days at which time the skins were completely penetrated, and dried cuttings indicated solid leather. The tanning solution has risen to 7.3 and was

then adjusted to pH 6.8 with five parts of a 10% lactic acid solution and agitation continued for two more days. The leather was removed, washed in water at approximately 90° F., wrung thoroughly, oiled on the grain with neatsfoot oil, and hung to dry. The resulting leather was full, solid, and of a pleasing light brown color; it had a shrink temperature of about 190° F.

Example 3

A tanning solution similar to that of Example 2 was made up by adding 39.2 parts by weight of a 25% solution of a product prepared as in Example 1, to 59 parts by weight of water. This solution was adjusted to pH 7.0 with dilute (10%) caustic soda.

Forty nine parts by weight of pickled calfskin were de-pickled for one hour in five parts of sodium acetate and 2.5 parts of sodium chloride in 200 parts of water. The skins were then washed thoroughly to remove salt and acetic acid and they possessed a pH of 5.5.

The skins prepared as above were added to the tanning solution and agitated for one-half hour. At the end of this time the solution was found to have a pH of 7.3. Agitation was continued at this pH for 8 hours and the skins were then allowed to stand for approximately eight hours longer. The pH was adjusted from 7.3 to 6.95 over a period of 7.25 hours with 10% lactic acid. The sample was put back in the tanning solution and agitated for eight hours and then allowed to stand for an additional eight hours. The shrink temperature after a total of 40 hours was 184° F.

The leather was then removed from the tanning solution and washed and dried. The dried leather was wet back with water and oiled with an emulsion of 50 parts of wool grease, 30 parts of sulfonated neatsfoot oil, and 25 parts of 30 ct. neatsfoot oil by brushing on the grain and on the flesh surface. The leather produced was full, solid, and had a light brown color.

Example 4

Sixty-two parts of calfskin prepared as described in the preceding example were tanned in a similar manner with 24.8 parts of a 50% solution of a quinone/resorcinol condensation product prepared as in Example 1 but using 2.25 mols of quinone to 1 mol of resorcinol. The tanning agent solution was added to 99.2 parts of water and adjusted to pH 7.0.

After 20 hours in this tanning solution the leather had a shrink temperature of 188° F. This rose to 202° F. after 56 hours total time of immersion in the solution. The leather was then washed and brushed on the grain and on the flesh side with an emulsion of 33 parts of sulfonated neatsfoot oil and 67 parts of water. The final leather was full, solid, and had a pleasing brown color.

The amounts of tanning agent used in the last two examples correspond to about 20% of the quinone/resorcinol (solids basis) on the drained pickled weight. This is in excess over that required for tanning and satisfactory leather has been made using 10 to 15% solids on the drained pickled weight. Pickling is unnecessary for tannages according to the present invention since with the pH used (7.0) it is obviously not necessary. Commercially it will ordinarily be found desirable to use bated stock rather than pickled stock. Roughly, drained pickled weight is equivalent to 0.8, the white, bated weight.

While I have shown certain illustrative compositions, products, and processes, it will be understood that without departing from the spirit of my invention one skilled in the art may readily prepare quinone/resorcinol polymerization products and may readily devise numerous tanning processes employing such products.

This application is a continuation-in-part of my application Serial No. 589,695 filed April 21, 1945, now abandoned.

I claim:

1. A polymeric tanning compound prepared by a process comprising effecting reaction of quinone with resorcinol in the presence of a solvent and an acidic polymerization catalyst, the reaction being continued until exothermic reaction is completed, the reactants then being refluxed for at least one-half hour and the polymer recovered, said polymer being a solid having at least ten six-carbon (C_6) rings, some of the six-carbon rings containing two oxygen atoms in para relation and substantially all the remaining six-carbon rings containing two oxygen atoms in meta relation, the ratio of the first-mentioned rings to the second being 1.5:1 to 2.5:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

2. A polymeric tanning compound prepared by a process comprising effecting reaction of quinone with resorcinol in the presence of a solvent and an acidic polymerization catalyst, the reaction being continued until exothermic reaction is completed, the reactants then being refluxed for at least one-half hour and the polymer recovered, said polymer being a solid having at least ten six-carbon (C_6) rings, some of the six-carbon rings containing two oxygen atoms in para relation and substantially all the remaining six-carbon rings containing two oxygen atoms in meta relation, the ratio of the first-mentioned rings to the second being 1:1 to 3:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

3. A polymeric tanning compound prepared by a process comprising effecting reaction of quinone with resorcinol in the presence of a solvent and an acidic polymerization catalyst, the reaction being continued until exothermic reaction is completed, the reactants then being refluxed for at least one-half hour and the polymer recovered, said polymer being a solid having at least ten six-carbon (C_6) rings, some of the six-carbon rings containing two oxygen atoms in para relation and substantially all the remaining six-carbon rings containing two oxygen atoms in meta relation, the ratio of the first-mentioned rings to the second being 0.6:1 to 4:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

4. In a process for the tanning of skins the step comprising subjecting a skin to the action of a polymeric compound prepared by a process comprising effecting reaction of quinone with resorcinol in the presence of a solvent and an acidic polymerization catalyst, the reaction being continued until exothermic reaction is completed, the reactants then being refluxed for at least one-half hour and the polymer recovered, said polymer being a solid having at least ten six-carbon (C_6) rings, some of the six-carbon rings containing two oxygen atoms in para relation and substantially all the remaining six-carbon rings

containing two oxygen atoms in meta relation, the ratio of the first-mentioned rings to the second being 1.5:1 to 2.5:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

5. In a process for the tanning of skins the step comprising subjecting a skin to the action of a polymeric compound prepared by a process comprising effecting reaction of quinone with resorcinol in the presence of a solvent and an acidic polymerization catalyst, the reaction being continued until exothermic reaction is completed, the reactants then being refluxed for at least one-half hour and the polymer recovered, said polymer being a solid having at least ten six-carbon (C₆) rings, some of the six-carbon rings containing two oxygen atoms in para relation and substantially all the remaining six-carbon rings containing two oxygen atoms in meta relation, the ratio of the first-mentioned rings to the second being 1:1 to 3:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

6. In a process for the tanning of skins the step comprising subjecting a skin to the action of a polymeric compound prepared by a process comprising effecting reaction of quinone with resorcinol in the presence of a solvent and an acidic polymerization catalyst, the reaction being continued until exothermic reaction is completed, the reactants then being refluxed for at least one-

half hour and the polymer recovered, said polymer being a solid having at least ten six-carbon (C₆) rings, some of the six-carbon rings containing two oxygen atoms in para relation and substantially all the remaining six-carbon rings containing two oxygen atoms in meta relation, the ratio of the first-mentioned rings to the second being 0.6:1 to 4:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

JOSEPH S. KIRK.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
644,482	Wartenberger	Feb. 27, 1900
2,404,711	Hoffmann	July 23, 1946

FOREIGN PATENTS

Number	Country	Date
96,565	Germany	Feb. 26, 1898

OTHER REFERENCES

"The Chemistry of Leather Manufacture" by J. A. Wilson, 2nd ed., vol. II, page 765, published 1929 by the Chemical Catalog Co., N. Y. C.

Pummerer et al., *Berichte Deut. Chem. Gesel.*, vol. 60B, 1927, pages 1442 to 1451.