

UNITED STATES PATENT OFFICE

2,469,438

QUINONE-RESORCINOL TANNING AGENT
AND PROCESSJoseph S. Kirk, Newtown, Pa., assignor to E. I.
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Del., a corporation of DelawareNo Drawing. Application April 23, 1946,
Serial No. 664,430

6 Claims. (Cl. 8-94.33)

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This invention relates to reduction products of interpolymerization products of quinone with resorcinol and is further directed to tanning compositions containing them; 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.

It is an object of this invention to provide novel chemical substances by the reduction of the interpolymerization products of quinone and

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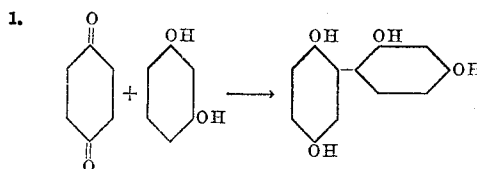
resorcinol. It is a further object to provide processes for the production of such reduced condensation products. It is a still further object to provide tanning compositions employing such reduced condensation products either alone or in conjunction with known tanning materials to treat skins and hides 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 reduced products of an interpolymerization product of quinone, that is benzoquinone, with resorcinol, and by the use of such a reduced 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:

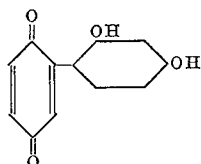


This product is highly soluble in water, and has no tanning action or precipitating action on proteins. By the use of oxidizing agents it can be converted to mon-resorcylic quinone which is

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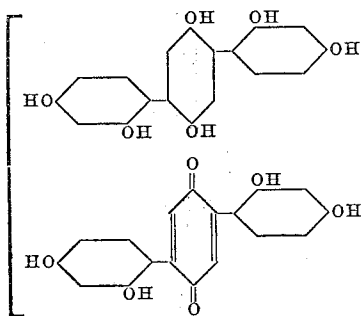
water-insoluble and therefore not adapted to use in tanning. The oxidized product has the formula:

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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 diresorcyl quinhydrone; in other words, a complex comprising an equimolecular mixture of diresorcyl hydroquinone and diresorcyl 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 produced from polymers unlike the compounds obtained by any of the procedures outlined above. The polymers 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 this invention are reduction products of 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 the preparation of reduced products for tanning have from about twelve to eighteen benzene rings in the molecule. The polymers are further characterized by the fact that they contain an average of two oxygen-containing groups for each benzene ring. The reduction products are similarly characterized.

The products of this invention, like the polymers from which they are produced, are water-soluble, are amorphous, and are precipitated by acids. The polymers are produced by processes under conditions which effect polymerization and the polymer is thereafter reduced. The polymers are themselves 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 polymers which are reduced to produced products of the invention it will be understood that the polymerization of quinone with resorcinol 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

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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.

5 With further reference to the structure of the reduced polymer of the invention it will be understood that the recurring six-membered rings which contain two oxygen groups, as those in a para relationship derived from quinone, will be in a lower state of oxidation than in the polymer itself. The oxygen may be present almost entirely as a hydroxy group.

15 Fortunately, the polymers from which reduced compounds of the invention are prepared can easily be differentiated from 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 made by reducing products 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.

25 The polymerization of quinone with resorcinol may be carried out in any of the various 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.

40 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.

45 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.

50 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.

55 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, 60 a half hour. The polymer produced is then separated from the reaction mixture by removal of the solvent.

65 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, 70 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, 75 pH 7.5.

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The ratio of quinone to the resorcinol is an important consideration in the preparation of polymers for use in preparing reduced products of the invention. Polymers of ratios from 0.6:1 to 4:1 have been prepared and their reduction products 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.

The reduction of polymers, as above described, to produce products of the invention may be effected by treatment with a reducing agent such as sodium bisulfite. As a matter of fact, it may even be found convenient to sell the products as bisulfite addition products. 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 as by catalytically reducing with hydrogen.

Leather produced using a reduced polymer according to the invention has a lighter color than that produced by using the polymer itself.

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 I

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

	Parts by weight
Quinone (2 mols)	216
Resorcinol (1 mol)	110
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% solu-

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tion (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 the 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.

The polymer produced according to this example 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 from 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 percent 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
	Per cent		
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

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A product prepared as in this example 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.

Example IA

A reduced product of the invention was prepared using a polymer made as above. A solution was made up with the following:

Parts by weight	
Quinone/resorcinol polymer (50% solids)	40
Water	40
Acetone	16
Hydrochloric acid (22° Bé. HCl)	5.9

Zinc was added to this solution, under an atmosphere of nitrogen, until no further color change was observed. Excess zinc was then removed by decanting. A small portion of NaHCO_3 was added and the solution settled into two layers. The upper aqueous layer was separated and used for tanning.

Depickled calfskin was tanned in a solution prepared as above and at a pH of 6.4 for a period of 96 hours. The leather produced had a shrink temperature of 206° F., and was white and had good character. The tannage was effected under an atmosphere of nitrogen. It was found that upon exposure to air or sunlight for any length of time the color of the leather changed to a light pink or reddish shade.

Example II

Using a polymer prepared as in Example I, a solution was made up of the following:

Parts by weight	
Quinone/resorcinol polymer (50% solids)	40
Water	120
Acetone	24

This solution was treated with one part by weight of NaHCO_3 and five parts by weight of stannous chloride. The precipitated stannic hydroxide was filtered from the solution and the solution used for tanning.

A tanning solution was made up using 20% of the tanning agent prepared as above, a depickled skin was put in the solution, and tanned under an atmosphere of nitrogen for ninety-six hours. The leather produced was light gray in color and had a shrink-temperature of 190° F.

Example III

A quinone/resorcinol polymer prepared as in Example I was treated with 10% (by weight) of solid sodium bisulfite and heated to the boiling point for fifteen minutes. Twenty per cent by weight of this product was used with water in a tanning drum for the treatment of depickled calfskin over a period of twenty-four hours. The leather had a shrink temperature of 204° F. (at complete penetration) and had a slight reddish color. The tanning agent was added in increment of 5% based on the dry pickled weight of the leather over a period of four hours at a pH ranging from 5.5 to 6.5.

The reduction products of polymerization products as 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 goat-skin and calfskin, and also skins of fur-bearing animals. It will naturally be necessary to adapt

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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 depickled 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.

Products of the invention as prepared 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 2,205,832 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.

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

I claim:

1. A tanning compound comprising a reduction product of a polymer which is prepared by a process in which quinone and resorcinol are reacted 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, 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 1.5:1 to 2.5:1, said polymer being further characterized as water-soluble, amorphous, precipitated by acid, and able to precipitate gelatin.

2. A tanning compound comprising a reduction product of a polymer which is prepared by a process in which quinone and resorcinol are reacted 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, 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.

3. A tanning compound comprising a reduction product of a polymer which is prepared by a process in which quinone and resorcinol are reacted 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, 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.

4. In a process for the tanning of skins the step comprising subjecting a skin to the action of a reduction product of a polymer which is prepared by a process in which quinone and resorcinol are reacted 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, 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 1.5:1 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 reduction product of a polymer which is prepared by a process in which quinone and resorcinol are reacted 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, 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 reduction product of a polymer which is prepared by a process in which quinone and resorcinol are reacted 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, 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.

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