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PROCESS FOR THE RETANNING OF MINERAL-TANNED LEATHERS

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11 Claims. (Cl. 8-94.21)

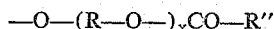
The present invention relates to and has as its objects a retanning process for mineral tanned leathers and is concerned with the use of water-soluble to dispersible compounds for this purpose, which are formed from phenol-resins or polyhydric phenols by substitution of the phenolic hydroxyl-groups by radicals of the general formula



or also possibly partially by radicals of the general formula



and/or



In the above formulae R stands for an aliphatic hydrocarbon radical preferably of 2-3 carbon atoms, R' stands for an aliphatic or aromatic hydrocarbon radical, R'' stands for a radical same as R' but preferably for an aliphatic hydrocarbon radical with at least 8 carbon atoms, x stands for a whole number between 1-10, preferably between 1-3, y stands for 1 or 2 and Me is an alkali-metal-, ammonium- or an amine-cation.

It is sometimes advantageous but not always necessary to add acids or compounds which react acidic with water, before, during or after the treatment of the pretanned leathers, when treating them further in the inventive way.

The products according to the present invention are not tanning materials as such or in the sense of a vegetable or synthetic tanning material. They are only useful for the treatment of leathers, preferably of mineral-tanned leathers. By the inventive treatment the character of leathers may be changed advantageously which is not or only difficultly possible with usual vegetable or synthetic tanning materials. But even if the change of the character of the leather by such inventive treatment is different from the type obtained by retanning with vegetable or synthetic tanning materials, we shall call also the inventive treatment a retanning process.

Towards mineral-tanned leathers the aforementioned inventively used products possess a very good affinity although their own tanning power is small. By the retanning process with these products the fullness, the fastness of grain and the softness of mineral-tanned, preferably of chromium-tanned leathers are greatly improved. The typical properties of mineral-tanned leathers, e.g. their fine grains are not at all or only little influenced. These properties—as it is known—are more or less changed in an undesired manner if commercial vegetable or synthetic tanning materials are used. Leathers treated with products according to the present invention distinguish themselves by good or very good non-fadingness, and the color of chromium leather is very much brightened up in a desirable way.

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Salts of condensation products of polyvalent organic acids with polyvalent aliphatic alcohols which are not substituted by aromatic radicals and which contain free, non-esterified carboxylic groups and of which the alkali metal- or ammonium salts are water-soluble, recently became known as auxiliary agents for textiles. In the leather field, especially for the retanning of leather, however, these products are not at all or only very little suitable. It was not to be expected therefore, that the inventive products which contain aliphatic alcohols of certain aromatic radicals are suitable for the retanning of leather.

The inventive products for a retanning process can be produced in ways known in principle.

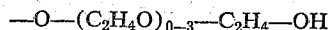
Phenol-resins or polyvalent phenols in the meaning of this invention especially may be:

(a) Compounds which contain several phenolic hydroxyl groups in an aromatic radical, e.g. hydroquinone, resorcinol or 1,5-dihydroxynaphthalene and

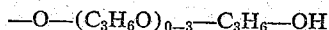
(b) Aromatic nuclei which are connected with other aromatic compounds in different ways by different bridges and which contain at least one phenolic hydroxyl-group per aromatic radical, e.g. novolaks, dihydroxy-diphenyl-sulfone, and the like.

Especially suitable for the production of the inventive retanning materials are novolaks, especially those from phenol or substituted phenols and 0.5-0.8 mol formaldehyde per mol of phenol used, and bisphenols such as dihydroxydiphenyl-methane, 4,4'-dihydroxy-diphenyl-dimethyl-methane or dihydroxy-diphenyl-sulfone. But the present invention also includes products which can be obtained from polyvalent phenols, as they are formed, e.g., by combining 2 mols of 4,4'-dihydroxy-diphenyl-dimethyl-methane by 1 mol of epichlorohydrine or by combining several phenol molecules with sulfone-, sulfonamide-, carbonyl-, urethane- or urea-groups.

The inventively modified phenol-resins or polyhydric phenols may be obtained by known methods e.g. by reacting the aforesaid novolaks or bisphenols with alkylene oxides, such as ethylene-oxide, propylene-oxide, butylene-oxide, or styrene-oxide or with chlorohydrines, such as ethylene chlorohydrine, propylene chlorohydrine or higher alkylene-chlorohydrines and by a following condensation thereof with polyhydric organic acids. Very suitable products are obtainable from novolaks or bisphenols of which the phenolic hydroxyl-groups are substituted by the radicals



or



The starting materials for the production of very effective retanning materials are obtained by the reaction of novolaks or bisphenols according to known methods with about 1.2-2.0 mols of ethylene- or/and propylene-oxide per OH-equivalent of the phenolic compounds. Other suitable products are also obtainable by the condensation of arylhydroxy alkanols, e.g. phenoxyethanol with an aqueous formaldehyde solution in the presence of acidic catalysts.

Polyhydric organic acids for the production of the inventive retanning materials are glutaric acid, adipic acid, terephthalic acid, maleic acid or succinic acid. Thus e.g. novolaks or bisphenols reacted with alkylene-

oxides are reacted with phthalic anhydride or with maleic anhydride by melting them together whereby acidic phthalic acid or maleic acid esters are obtained. Suitable retanning materials are obtained by esterifying all or only a part of the OH-groups of such modified phenol-resins with the aforesaid polyhydric organic acids.

Retanning materials according to the present invention are also obtained by reacting part of the OH-groups of the modified phenol-resins or polyhydric phenols with monovalent organic acids, especially with long chain acids such as stearic-, palmitic- or oleic acid. Preferably a larger part however should be reacted with polyhydric organic acids. In each case the esterified products should contain an essentially great number of free, non-esterified carboxylic groups, so that they may be soluble in water or at least dispersible in form of their alkali metal-, ammonium- or amine-salts and it is especially suitable to use these alkali metal salts, especially the sodium or the potassium salts, as well as the ammonium salts of the inventive condensation products for the retanning process.

The retanning materials useful according to the present invention if they do not contain any other water-solubilizing groups beside the carboxyl groups, as e.g. sulfonic acid radicals, are precipitated from their aqueous solutions with acids or acidic reacting metal salts, as e.g. the chromium-, aluminum- or zirconium salts, in aqueous solutions.

As said above, the condensation products according to the present invention are suitable for retanning of mineral tanned leathers, especially of leathers, which were tanned with chromium- or/and aluminium tannics. The retanning of the leathers is carried out according to methods known in the art, e.g. by milling the leather with an aqueous solution of the condensation products in the drum. The retanning is preferably carried out at room temperature, but possibly sometimes also at a higher temperature, e.g. between about 50–60° C. Retanning may also be carried out sometimes with the inventive condensation products in powder form, i.e. without water by milling the wet raw leathers. Usually about 1–6 parts by weight of the inventive products are used per 100 parts by weight of wet leather.

It may also be of advantage to acidify the retanning liquor before or during the retanning process, especially if the leathers only are slightly acidic. Acids like formic acid, acetic acid or boric acid or compounds which react acidic in aqueous solutions, such as bisulfites, chromium-, aluminium- or zirconyl salts are useful there. The acidity of the leather is usually sufficient if the pH-value is less than 7 and preferably is about 4.5–6.0 after the retanning process. The quantity of the acid or of the acidic compounds which may be added to the tanning liquor after or during the retanning, is preferably calculated so that the pH-rate of the retanning liquor is adjusted at the end of the retanning to a degree where the inventively used retanning products are completely or almost completely precipitated. This usually is the case at a pH-rate of the tanning liquor of 4.5–5.5.

The condensation products useful according to the present invention also may be used together with anionic or non-ionic tanning, retanning or resin-tanning materials or other impregnating materials as well as dyes. Also the retanning process may be carried out in combination with the treatment of the leathers with known cationic, anionic or non-ionic tanning, retanning or resin-tanning materials.

The further processes to obtain finished leathers from the inventive tanned leathers are carried out according to known methods.

Example 1

100 parts by weight of chromium-tanned calf-leather, which has an average pH of about 3.8, is milled in a drum with about 250 parts by weight of water at 20–35°

C. and with 0.4–0.6 part by weight of sodium bicarbonate.

After about 1–5 minutes between 3–5 parts per weight of the retanning material described below are added in the form of a powder.

The consumption of the liquor may be seen from the degree of precipitation or turbidity after the addition of acid to the liquor. After milling for about 45–75 minutes usually most of the product is taken up by the leather. The remaining liquor, which shows a pH value of 5.3–5.8 is removed. After washing the leather with luke warm water of about 50–60° C. it may be dyed in a new dye-bath in the usual manner, it then is greased and completed in the usual way. There is obtained a full and tight grain leather, which distinguishes itself by a fine grain, light color and very good light resistance.

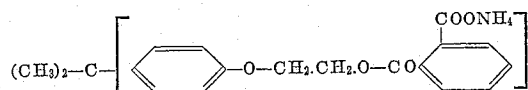
The product used for the retanning can be obtained in the following manner:

150 parts per weight of an anhydrous, ethoxylated novolak which is obtainable by reaction of about 100 parts by weight of a novolak obtained in the presence of an acidic condensation material from phenol and formaldehyde in a molar proportion of about 1:1.55 with about 60 parts by weight of ethylene oxide, are heated to about 110° C. To the hot melt there are added 150 parts by weight of phthalic acid anhydride while stirring. The mixture thereby is kept at a temperature of 120–125° C. for half an hour. After cooling the clear melt to about 100–105° C. there is added slowly while stirring a warm solution (of about 30° C.) of 54 parts by weight of sodium carbonate in 180 parts by weight of water. There are added further 100 parts by weight of water to the clear solution and possibly some sodium hydroxide, too, so that the solution shows a pH-value of about 7 at the end at the dilution of 1:10. The water soluble and acid precipitable product then is spray-dried.

Similar products are obtained if a starting material is used which contains a corresponding novolak on a cresol base instead of the above said phenol-novolak.

Example 2

Retanning is carried out as described in Example 1, but using instead of the retanning-material mentioned therein 6–10 parts by weight of a 50% aqueous solution of the compound of the following formula



There are obtained very full and light leathers of excellent quality. The color of the leather is the lighter the more the leather contained acids before retanning and the smaller therefore the quantity of employed bicarbonate was.

Example 3

100 parts by weight of a neutralized calf-leather tanned with commercial chromium or aluminium-tanning-materials and which shows an average pH of about 5.5 is washed with water of a temperature of 50° C. Thereafter it is milled for about 30 minutes in a drum with about 150 parts by weight of water of a temperature of 50° C. and 8–10 parts by weight of an about 50% aqueous solution of retanning material obtained in the manner described below.

Then there is added formic acid to the liquor so that it shows a pH of about 5. After a further period of 15 minutes in the drum the leather is fat-liquored in the usual manner in the same liquor. After completion of all further usual treatments there are obtained full, fast-grain, light and fadeless leathers.

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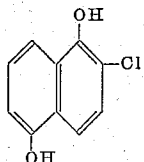
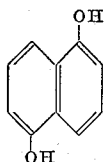
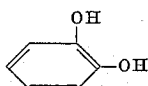
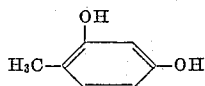
The product used as a retanning-material is prepared as follows:

A novolak produced in the usual and known way in the presence of hydrochloric acid from o-cresole and formaldehyde in a proportion of 1:0.6 mol are further reacted in usual manner in the presence of a catalytic amount of sodium hydroxide with about 1.2–1.3 mols or propylene oxide per OH-equivalent of the novolak.

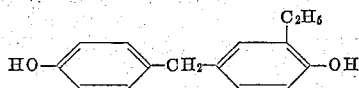
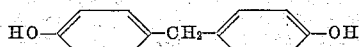
The reaction product then is melted with 1 mol of maleic acid anhydride per OH-equivalent of the oxalkylated novolak at 120° C. for about 30 minutes. After cooling to about 100° C. the reaction product is diluted with a concentrated ammonia-solution. The yellow-brownish clear solution then is further diluted with water to a concentration of about 50% and brought to a pH of about 7.5 (1:10 diluted with water) by adding further amounts of ammonia, if necessary.

Instead of the before described retanning-material a corresponding product may be used which was after the dilution with ammonia heated to about 100° C. for about 30 minutes with 0.5 mol of sodium-bisulfate per mol of used maleic acid-anhydride.

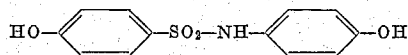
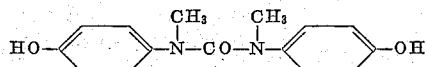
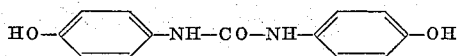
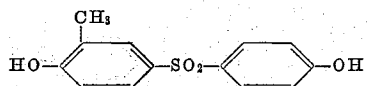
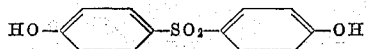
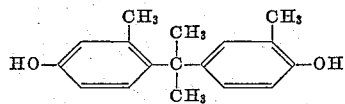
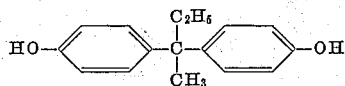
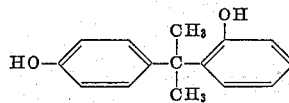
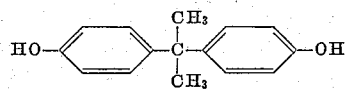
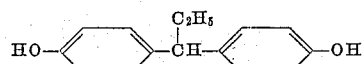
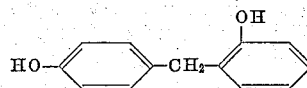
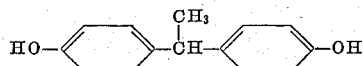
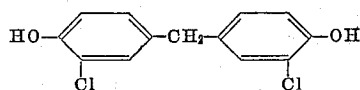
Other reaction products of same or similar properties may be obtained from the following polyhydric phenols:

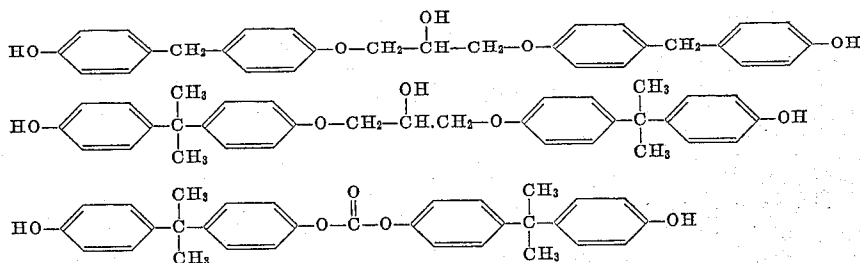


and from the following poly-phenols:

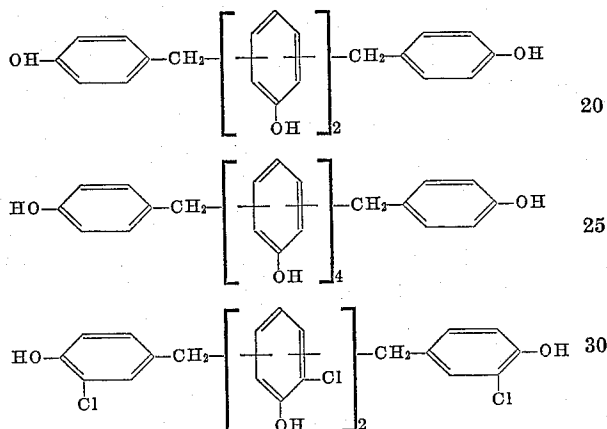


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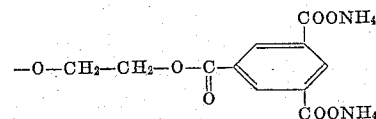
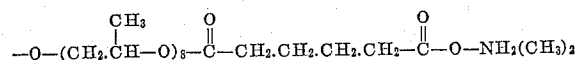
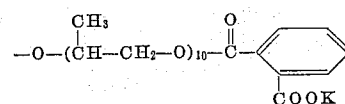
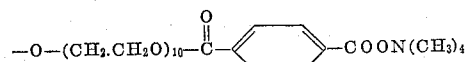
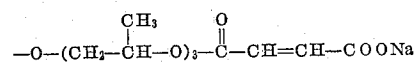
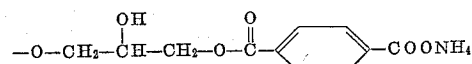
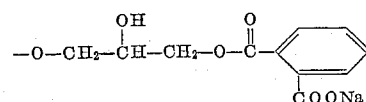
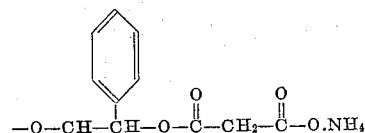
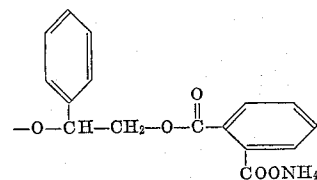
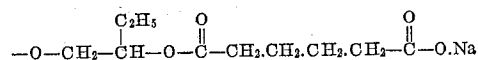
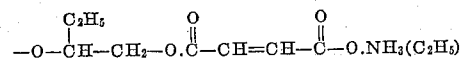
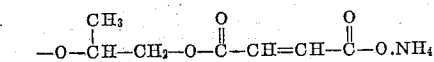
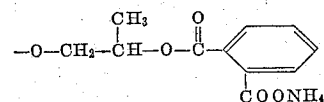
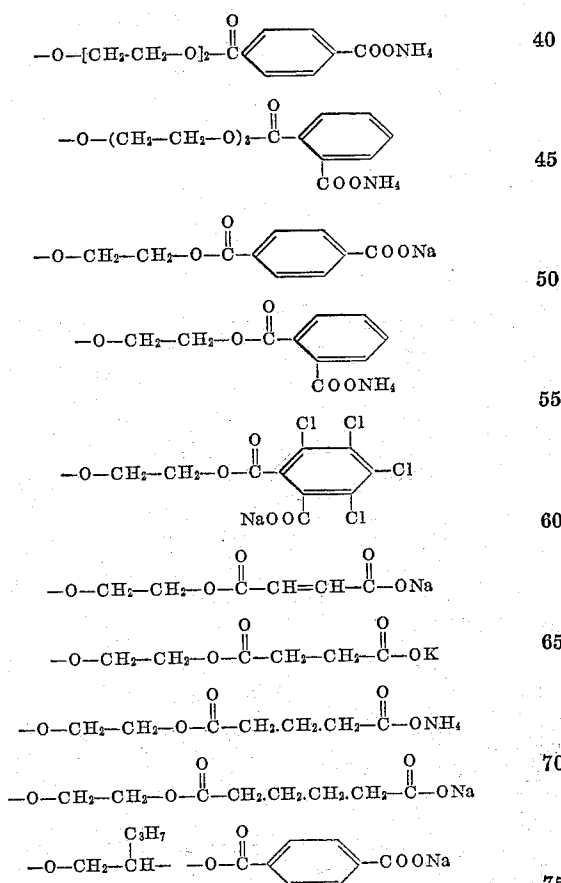




The above poly-phenols also lead to reaction products in the meaning of this invention. At last the following novolaks should be mentioned as examples for phenols of such type to give inventively useful retanning agents: 15



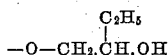
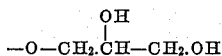
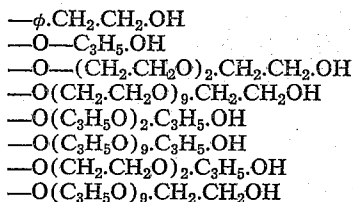
As examples for the second part of the molecule which gives useful products in the meaning of this invention the following esterified glycol- and poly-glycol-esters may be mentioned: 35



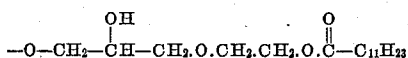
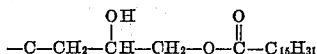
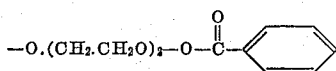
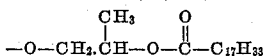
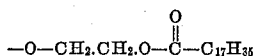
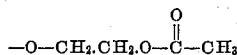
All these above mentioned radicals which may be attached to the phenols stated above give water soluble or water dispersible compounds in the meaning of this invention if they are present in the salt form indicated above.

As stated before, however, part of the radicals attached to the phenols may be present in a state of non-esterified glycols and poly-glycols as it may be shown by the follow-

ing formulae which are only given for exemplifying purposes and not to limit the scope of invention thereto:



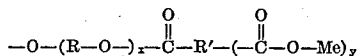
As further stated above the afore-mentioned free glycols can be esterified also by normal fatty acids as it may be seen from the following list where some examples are given to illustrate this:



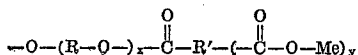
It has to be understood, however, that the two last mentioned groups of compounds should be present only in such an amount that the resulting mixture does not become water insoluble or non-dispersible. Usually the amount of the last two classes of substituents of the OH-group should not exceed 50-70%, but as it is easily to be seen for a person skilled in the art, the amount of the last two classes of substituents largely depends on the nature of the before-mentioned esterified poly-glycol ethers containing carboxylic groups or their salts respectively.

We claim:

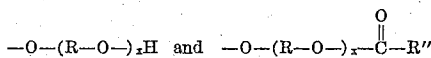
1. A process for the retanning of mineral-tanned leathers which comprises treating such leathers with water-soluble to water-dispersible compounds which are formed by substituting the phenolic hydroxyl groups of a member selected from the group consisting of a polyhydric phenol, a polyphenol, and a novolak by a radical selected from the group consisting of (a) a radical of the formula:



per se, and (b) a radical of the formula:



together with one additional radical selected from the group consisting of:



5 wherein R stands for a member selected from the group consisting of an aliphatic radical of 2-5 carbon atoms and a phenyl-substituted derivative of an aliphatic radical of 2-5 carbon atoms, and R' and R'' represent a member selected from the group consisting of an aliphatic radical of up to 20 carbon atoms and a phenyl group, x is a whole number between 1 and 10, y is a number from 1-2, and Me is a member selected from the group consisting of an alkali metal and an ammonium group.

15 2. A process for the retanning of mineral-tanned leathers according to claim 1 wherein said leathers are treated with those compounds of claim 1 wherein the phenolic part of the molecule is a bisphenol.

3. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the phenolic part of the molecule is a dihydric phenol.

20 4. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the phenolic part of the molecule is a novolak containing up to 5 phenolic nuclei.

5. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the alkylene oxide bridge of the molecule consists of 1-3 ethylene oxide molecules.

6. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the alkylene oxide bridge of the molecule consists of 1-3 propylene oxide molecules.

7. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the acid part of the molecules is phthalic acid.

8. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the acid part of the molecules is terephthalic acid.

9. A process for the retanning of mineral-tanned leathers according to claim 1 which comprises treating such leathers with those compounds of claim 1 in which the acid part of the molecule is maleic acid.

10. The process of claim 1 wherein acids or compounds which react acidically in an aqueous solution are added to the retanning liquor either before, during, or after the retanning so that after the completion of the returning treatment, the leathers will have a pH value of less than 7.

11. The process of claim 10 wherein said pH value of the leather is about 5.5-6.5 after the completion of the treatment.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,101,237

August 20, 1963

Wolfhard Luck et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 9, line 4, for " $-\phi.CH_2.CH_2.OH$ " read
-- $-O.CH_2.CH_2.OH$ --.

Signed and sealed this 26th day of May 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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