EUROPEAN QUALIFYING EXAMINATION 1999

PAPER A
CHEMISTRY

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CLIENT'S LETTER

Ladies and Gentlemen:

We have invented novel synthetic tanning agents. Synthetic tanning agents are often called syntans. The syntans hitherto used in the tanning of animal hides (skins) still require further improvements with respect to the tanning process and often with respect to the properties of the leather obtained in this process. Important properties of leather are e.g. the softness, plumpness, water and light resistance. To achieve the desired properties, a number of additional treating agents such as fats, oils, lubricants, dyes, waxes and lacquers are used in the leather industry individually or in combinations. As known, these treatments serve to prevent rotting and putrefaction under humid conditions and to achieve, improve or control the properties of the leather. Various types of leather have thus been obtained with a broad variety of properties.

The hides are pretreated in the usual way, as necessary in accordance with the origin of the hide and the intended leather product. Then they are usually treated with aqueous solutions of tanning agents in acidic conditions to ensure an efficient processing speed and quality. The tanning agents convert the proteins in the hides into the crosslinked leather material. Stable aqueous solutions of the tanning agents are indispensible for efficient tanning or retanning processes. Under no circumstances should any precipitates be formed in these solutions during their use, because these may form on or inside the hides, cause uneven products and are very difficult to remove from the leather. In short, precipitates impair the leather quality.

Our invention relates to particular syntans which can be used efficiently to tan animal hides or to modify leather which has already been tanned (ie. "retanning") e.g. by means of chromium compounds. Our syntans meet the above-mentioned requirements. Moreover, they have another advantage in that they are based on commercially available starting compounds already used for this purpose.

Similar to other well-known syntans, our agents are sulphonated polycondensation products derived from hydroxyaryl sulphones, aromatic sulphonic acids and formaldehyde. The presence and the positions of any

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lower alkyl substituents in the aromatic components do not matter as long as the products do not crystallise or precipitate from their aqueous solution before or during their use.

You are not familiar perhaps with the different types of compounds as referred in our letter. Therefore we would like to give you a brief summary of the general structures of such compounds. In the corresponding structural formulae, **Ar** refers to an unsubstituted or substituted aryl group at each occurrence.

Compounds of the type **Ar-OH** are called hydroxyaryl compounds or phenols, e.g. phenol (hydroxybenzene) itself: $\mathbf{C_6H_5OH}$. Aromatic sulphonic acids have the general structural formula $\mathbf{Ar\text{-}SO_3H}$, and aromatic sulphones are compounds of the general structural formula $\mathbf{Ar\text{-}SO_2\text{-}Ar}$. The sulphates comprise the anion of the formula $\mathbf{SO_4^{2-}}$, the sulphite anion has the formula $\mathbf{SO_3^{2-}}$. When we refer to "partly" or "partially sulphonated phenol", it is intended to mean mixtures of the initially charged, unreacted phenol and of the hydroxyphenyl sulphonic acid (= hydroxybenzene sulphonic acid) which may be formed in the reaction of the phenol with sulphuric acid.

Before turning back to our invention, some further explanations referring to different polycyclic aromatic ring systems are added here for your convenience: Polycyclic aromatic compounds include at least two aromatic (e.g. benzene) rings directly bonded to each other. The simplest "uncondensed" compound of this type is biphenyl ($\mathbf{C_6H_5\text{-}C_6H_5}$; one C-atom of the first ring is bonded to one C-atom of the other). "Condensed" or "fused" polycyclic aromatic compounds comprise at least two aromatic rings which share two vicinal (neighbouring) carbon atoms, e.g. naphthalene ($\mathbf{C_{10}H_8}$; two hexagons having a common edge).

The sulphones used in the preparation of our syntans are prepared from hydroxyaryl compounds, such as phenol and lower alkyl substituted phenols. Typical examples are bis(hydroxyphenyl) sulphones and bis-cresol sulphones. An excess amount of the hydroxyaryl compound is reacted with concentrated sulphuric acid at elevated temperatures. Depending on the molar ratio of the phenol and the sulphuric acid, some sulphonated phenol may form as a by-product (in general, in the form of hydroxyphenyl sulphonic acid). The crude product is then more or less neutralised and can be purified in order to avoid that certain amounts of residual hydroxyaryl compound and of the by-product are exceeded. This preparation is already known.

The second starting component are aromatic sulphonic acids, in particular those derived from polycyclic

The second starting component are aromatic sulphonic acids, in particular those derived from polycyclic aromatic compounds. Mixtures of such compounds are preferred wherein at least one component is derived from uncondensed and at least another is derived from condensed polycyclic aromatic compounds. Typical examples for the first type are biphenyl sulphonic acids, terphenyl sulphonic acids and quaterphenyl sulphonic acids, i.e. phenyl sulphonic acids wherein the phenyl has one or more phenyl substituents. Examples for the second type are sulphonic acids derived from naphthalene, anthracene or phenanthrene.

Any commercially available form of formaldehyde can be used which under the reaction conditions releases formaldehyde (CH_2O). Thus, paraformaldehyde will do.

The process will now be further described for a preferred embodiment. The ranges of molar ratios, temperatures and other conditions mentioned below are applicable to all embodiments of our invention. Of course, for further improved results, the conditions will have to be optimized for each combination of starting compounds within these ranges. The course of a reaction can be traced by analysis of samples from the reaction mixture to find out when the conversion is complete or has arrived at a satisfactory value. All this is well-known in the art.

In a procedure well-known in the art to prepare the sulphone, phenol can be reacted with concentrated sulphuric acid at temperatures of 165 to 200°C in a closed reaction vessel. In general, a temperature of 170 to 175°C will be sufficient.The reaction is stopped when the acid content has fallen to about 10% of the initial charge, e.g. by distilling off residual phenol (under reduced pressure) and allowing to cool. The residual sulphuric acid is neutralised by slowly pouring the reaction mixture into an aqueous alkaline solution to achieve a pH of 4 to 7. Part of the water in the aqueous solution evaporates at this stage. After cooling, the crude product is a dispersed mixture of bis(hydroxyphenyl) sulphone, some partially sulphonated phenol and inorganic sulphate. The sulphone can easily be recovered from the reaction mixture as it is the least soluble component. In order to obtain the sulphone, mainly bis(4-hydroxyphenyl) sulphone, in a satisfactory yield phenol is added to the sulphuric acid in a molar ratio of roughly (2 to 2.5):1.

The aromatic sulphonic acid component is prepared by sulphonating a mixture of naphthalene and the heavy fraction from the industrial production of biphenyl, mainly consisting of terphenyl, with concentrated sulphuric acid at temperatures of 130 to 170°C. The end of this reaction can easily be determined by testing the water-solubility of samples taken from the reaction mixture. The sulphonic acids are entirely water soluble contrary to the aromatic starting compounds. After the reaction the pH of the reaction mixture is adjusted with a basic compound to a value of 3 to 6. The product can be isolated.

The sulphonic acid and the sulphone components thus obtained are charged to a reaction vessel in the amounts given below. Then an aqueous solution of formaldehyde usually containing 20 to 40% of formaldehyde is added with stirring. The molar amounts of the reactants, per 1 mol of the uncondensed polycyclic aromatic sulphonic acid (**a**), in this initial reaction mixture should be:

b) the condensed polycyclic aromatic sulphonic acid	0.2 to 2 (preferably 0.5 to 1.6)
c) the sulphone	0.3 to 2 (preferably 0.5 to 1.5)
d) formaldehyde	0.65 to 5.5 (preferably 0.7 to 3.5)
e) phenol and hydroxyphenyl sulphonic acid (expressed as one amount)	0 to 1, (preferably less than 0.1)

This mixture is heated to at least 60°C, but below the boiling point for a period of, in general, 10 minutes to 3 hours. Preferably the reaction is carried out for 30 minutes to 2 hours at a temperature in the range of 80°C up to a temperature just below the boiling point of the mixture.

In the absence of the condensed polycyclic aromatic sulphonic acid (**b**), the uncondensed polycyclic aromatic sulphonic acid (**a**) and the sulphone (**c**) were found to react with formaldehyde (**d**) to give inhomogeneous, partly water insoluble products. As indicated above, insolubles make the product unsuitable for our purposes. Insolubles are often obtained as well, when the partly sulphonated phenol (**e**) is present in the reaction mixture. To diminish this risk, the amount of the partly sulphonated phenol (**e**), if present, should not exceed an amount of half the amount of the condensed polycyclic aromatic component **(b)** and, at the same time, the formaldehyde **(d)** should be charged in such an amount that the initial molar ratio of the aldehyde to the partly sulphonated phenol **(e)** is at least about 1.25:1.

It is possible to remove the above mentioned precipitates, e.g. by filtration, only with undue effort. Their disadvantageous effects can however be reduced by reacting the reaction mixture containing these solids in an additional step with an aqueous solution of a sulphite **(f)** such as sodium hydrogen sulphite and additional formaldehyde at a temperature of 80 to 120°C for another 30 minutes to 5 hours at a pH value of 4 to 8. The molar ratio of the said partly sulphonated phenol **(e)** to sulphite **(f)** should be below 1:1, preferably (0.4 to 0.7):1. The molar ratio of phenol **(e)** to formaldehyde in this reaction step should be 1:(1 to 2.5). This additional modification can also be carried out when the reaction mixture is free of any partly sulphonated phenol **(e)**. The solubility of the syntan can be further increased in this way so that homogeneous solutions having higher solids content become possible.

An indication of its stability against precipitation is the fact that the syntan forms homogeneous aqueous solutions with a solids content of up to 50% by weight. The product can be dried to a brittle solid, which can easily be redissolved. The above procedure allows a particularly good pH control, it can be carried out in a single reaction vessel, and the danger of obtaining insoluble resin-like products is at least greatly diminished.

Our primary goal was to find a product which does not precipitate from its aqueous solution at any stage of the normal tanning procedure. The product can also be used as a finishing agent or retanning agent for leather tanned with mineral tanning agents; it can also be used to brighten chromium-tanned leathers. From a practical point of view, it can be said that the leathers tanned or retanned with our compositions are equivalent to the leathers in the market tanned or retanned with other syntans. Outstanding plumpness and softness and an exceptionally good fastness against light are characteristic for the leathers tanned or retanned with our compositions.

The fact that one can make concentrated aqueous solutions of our syntans without the production of precipitates allows shorter tanning times to be used.

As usual, tanning is always carried out at pH-values of 3 to 6. When the syntan is to be used as a finishing (retanning) agent, a pH-value around the neutral value of 7 has proven to be useful.

It should be evident that the product cannot or can hardly be defined by a chemical formula, because the reactions are not strictly stoichiometric. The syntan product consists of a complex mixture of compounds. The solutions of the syntan products can be used optionally together with aliphatic and/or aromatic monocarboxylic or dicarboxylic acids and/or ammonia or amines for further pH control.

The lower alkyl groups comprise up to C_4 alkyl. Percentages in the following examples, which we have enclosed to further elucidate our invention, relate to the weight (mass) unless stated otherwise.

Example 1

In a closed stirred apparatus which is provided with a reflux condenser and thermometer, 230 g (1 mol) of terphenyl were melted with 90 g (0.7 mol) of naphthalene at 120°C. 372 g of sulphuric acid monohydrate were then allowed to run in and sulphonation was carried out at 140°C for 3 hours, whilst stirring continuously. The mixture was then allowed to cool to 110°C and thereafter to run slowly into 300 g of diluted aqueous alkali hydroxide with external cooling. When the addition to the aqueous solution had ended, the pH value of the solution was 3.5 and its temperature was 80 to 90°C. 250 g (1 mol) of bis-(4-hydroxyphenyl) sulphone were introduced at this temperature and, thereafter, 120 g of an aqueous solution of formaldehyde (having a 30% strength, 1.2 mol) were added slowly whilst a constant temperature of 80°C was maintained. The condensation reaction was then allowed to proceed at 90°C, with continuous stirring. During this condensation reaction, the bis-(4-hydroxyphenyl) sulphone dissolved completely and the viscosity of the reaction mixture rose with the increasing degree of condensation. After a condensation reaction of about 3 to 4 hours, no free formaldehyde could be found and the reaction mixture was adjusted to the desired pH value of 3.5 to 4 with 45% strength aqueous sodium hydroxide solution for use as a syntan.

Example 2

As the product can also be used for re-tanning chromium-tanned leather, another batch otherwise identical to that of Example 1 was adjusted with aqueous ammonia to a pH value of 6.5.

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Example 3

Calf skins pretreated by methods customary in practice were treated in a tanning drum with 200% of a liquor which had a solids content of 25% of the condensation product of Example 1 and which had been partly neutralised to pH 3.5 and adjusted to an acid number of 100 by adding glacial acetic acid. After a total tanning time of 6 hours, the tanning agent was absorbed completely. After greasing, drying and mechanical working which are customary in practice, leather of excellent quality as regards plumpness and softness was obtained. It showed excellent resistance to fading due to light.

Example 4

Cow-hide leather chrome-tanned in the manner customary in practice, after rinsing thoroughly, was neutralised to a pH value of 5.2 to 6.8 in the moist leather. The liquor of the condensation product of Example 2 was then allowed to act on the leather in a rotating tanning drum. After about 30 minutes, the syntan was completely absorbed by the leather. Dyeing and greasing was then carried out in the customary manner. After drying and mechanical working which are customary in practice, leather with a very good plumpness, softness and brightening effect, excellent levelness and good light resistance was obtained.

Having regard to the fact that similar syntans have been well known for decades, see the two documents enclosed herewith, and that leather production is a common technique carried out all over the world, we see a danger in that, by chance, our invention might be repeated elsewhere. Therefore we ask you to prepare a European patent application very urgently and to file it as soon as possible, preferably by this week. Please make sure that our invention will be well protected by a valid European patent, since our competitors will almost certainly lodge an opposition against any patent granted for us, because even apparently minor improvements may result in a big commercial success in this heavily contested market.

Yours sincerely

Bright Hide Ltd.

DOCUMENT I (State of the Art)

Compounds having excellent tanning properties are obtained by heating aromatic sulphonic acids, formaldehyde and bis(hydroxyphenyl) sulphones in acidic to neutral solution. The poorly soluble sulphones dissolve in the course of the condensation reaction to give products which are miscible with water at any ratios. These products have good tanning properties in weakly acidic solution and the leather obtained therewith is light-resistant and has good physical properties.

The bis(hydroxyphenyl) sulphones are obtained by heating phenol in excess with concentrated or fuming sulphuric acid to temperatures of 160 to 190°C. The sulphones can be purified to remove phenol and any hydroxyphenyl sulphonic acid which is formed as a by-product by distillation of the phenol under reduced pressure and by crystallisation or precipitation of the sulphones from the concentrated aqueous reaction mixture utilising their poor solubility.

As an aromatic sulphonic acid, naphthalene sulphonic acid may be mentioned which is obtained by heating naphthalene and concentrated sulphuric acid to a temperature of 130 to 170°C until the product is entirely water-soluble.

The above sulphones are then heated with an equal amount of the above sulphonic acid, small amounts of water and formaldehyde for approximately 1 to 4 hours to temperatures of 100 to 130°C. The resulting products are easily soluble in water and give clear aqueous solutions. They give - similar to vegetable tanning materials - a strong precipitation with ferric chloride and can be recovered as a solid.

Example 1

In the first step 520 parts by weight of naphthalene and 560 parts by weight of concentrated sulphuric acid were heated for two hours at from 140 to 160°C until the water-soluble sulphonic acid had formed. In another vessel the sulphone component was prepared by heating 540 parts by weight of phenol with concentrated sulphuric acid to from 170 to 180°C for three hours. Thereafter residual phenol was removed by distillation.

100 parts by weight of the crude naphthalene sulphonic acid product, 100 parts by weight of the crude

sulphone product, 50 parts by weight of water and 45 parts by weight of 30 weight-% formaldehyde were heated to about 110°C for about an hour. The product can be dissolved in water to give a clear aqueous solution. For tanning, the solution was adjusted to weakly acidic by addition of alkaline solution (lye).

Example 2

Example 1 was repeated with the exception that tetrahydronaphthalene was reacted with concentrated sulphuric acid in the first step.

Both tanning products could be used in weakly acidic aqueous solution of up to 20% solids contents to tan cow hides. Leather of very high stability against light and humidity was obtained, at least of equal quality to leather obtained with vegetable tans.

Claim

Process for the preparation of tanning condensation products of bis(hydroxyphenyl) sulphones characterised in that unsulphonated bis(hydroxyphenyl) sulphones are heated together with formaldehyde in the presence of aromatic sulphonic acids in acidic aqueous solution.

DOCUMENT II (State of the Art)

Water-soluble compounds can be obtained by treating hydroxy group-containing aromatic compounds such as phenols with formaldehyde or with a combination of formaldehyde and a sulphite. Heating bis(hydroxyaryl) sulphones with the combination of formaldehyde and a sulphite under elevated pressure also gave water-soluble compounds. This reaction will be referred to here as "formyl sulphitation" for the sake of simplicity. Experiments to apply this formyl sulphitation reaction on the condensation products of bis(hydroxyaryl) sulphones and formaldehyde or on the condensation products of bis(hydroxyaryl) sulphones and aromatic sulphonic acids and formaldehyde result, in general, in water-insoluble products.

Surprisingly, it has now been found that the said condensation products of bis(hydroxyaryl) sulphones, formaldehyde and, optionally, an aromatic sulphonic acid, which have been prepared under specific reaction conditions, react more easily with formaldehyde and a sulphite than the starting sulphone compounds and give water-soluble products useful as tanning agents.

The condensation reaction between the bis(hydroxyaryl) sulphone, formaldehyde and, optionally, the aromatic sulphonic acid is carried out under weakly alkaline conditions (pH of about 8 to 10). Small amounts, such as 0.6 mols, of formaldehyde per 2 mols of sulphone require significantly longer heating of the reaction mixture than the reaction with greater amounts of the aldehyde, such as 1.25 mols per 2 mols of sulphone. The latter amounts may however increase the danger of a too high degree of condensation which impairs the solubility of the final products in water, even to the degree that they cannot be successfully converted to water-soluble tanning agents. Preferably as little water as possible is used, as long as the mixture can be stirred, and the reaction temperature is preferably kept at the boiling point of the mixture, e.g. up to 110 or 130°C. The best reaction conditions and molar ratios for the condensation reaction can easily be determined by a person skilled in the art by a few preliminary experiments so that in the formyl sulphitation reaction, which follows, the desired water-soluble products can be obtained.

In general, the formyl sulphitation reaction is carried out using 1 mol of a sulphite and 1 mol of formaldehyde for each mol of the sulphone initially used in the condensation reaction. Often mixtures of a hydrogen

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sulphite and a neutral sulphite are advantageously used. These compounds can be mixed together in such a way that no precipitates form when added to the reaction mixture. The formaldehyde is preferably used as an aqueous solution of about 30 weight-% strength.

The water-soluble products of the present process can be used efficiently as tanning agents in the preparation of leather from hides of various animals. The leather has a significantly improved light stability.

Example 1

m,m'-Dicresol sulphone (100 parts by weight) was heated with stirring in a mixture of 50 parts by weight of water and 23 parts by weight of sodium hydroxide to a temperature of 100°C. Then 16 parts by weight of formaldehyde were added as a 30 wt.-% solution, and the mixture was maintained at this temperature for two hours.

To this reaction mixture containing the condensation product of the above components, a concentrated aqueous solution prepared from 35 parts by weight of sodium hydrogen sulphite, 28 parts by weight sodium sulphite and 38 parts by weight of formaldehyde (30 weight % strength solution) was added with stirring and the pH value was adjusted to between 4 and 6. The reaction mixture was kept at the same temperature as above until the following test was positive. This was the case after a reaction time of about an hour. In the test, a sample of the reaction mixture was acidified with a strong mineral acid to precipitate the resin contained therein. The test was positive when the resin recovered from the mixture redissolved in water.

Then the whole reaction mixture was treated with mineral acid to precipitate the resin. The resin was recovered. For use it was redissolved in water and slightly acidified by adding an organic acid.

Example 2

In a similar way to that described in Example 1, 100 parts by weight of bis(hydroxyphenyl) sulphone were heated in admixture with 25 parts by weight of 30% aqueous sodium hydroxide solution, 15 parts by weight of additional water and 16 parts by weight of formaldehyde (30 wt.-% strength) for 5 hours to 100°C. After the condensation reaction, a concentrated aqueous solution of 26 parts by weight of sodium hydrogen sulphite, 35 parts by weight of sodium sulphite and 38 parts by weight of formaldehyde (30 wt.-% strength solution) was added, and the reaction mixture was further heated to 100°C at a pH of between 5 and 7 until the above test was positive (after about 5 hours). The product was recovered as described in Example 1.

Claim

A process for the preparation of water-soluble condensation products by pre-condensing bis(hydroxyaryl) sulphone with formaldehyde or a mixture of formaldehyde and an aromatic sulphonic acid at weakly alkaline conditions, and reacting the intermediate condensation product thus obtained with a mixture of formaldehyde and salts of sulphurous acid under atmospheric pressure at the boiling point of the mixture.