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(54) Title: LEATHER PRODUCTION

(57) Abstract: Application to leather of various leather treatment agents, in particular dyes, is improved by the use of materials such as substantially linear surfactants having amphoteric head groups.



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LEATHER PRODUCTION

The present invention relates to the production of leather, and in particular to the various treatments that a hide or pelt undergoes to convert it to a finished piece of leather. More particularly, the invention relates to the use of a material of a particular chemical structure to facilitate or to improve those treatments, in general by increasing the effect produced by a given leather treatment agent relative to the amount used or relative to the treatment time. In a preferred embodiment the colour yield of a dye is increased, thus allowing deeper colours to be achieved or to reduce quantities of dye consumed.

Before the invention is described in detail, a word may be said about terminology. Various processes are employed in transforming a raw hide into a finished piece of leather. The substrate to which these various processes are applied is known by various different names depending on the processes that have already been carried out. For example, the substrate is usually referred to first as a hide (or skin), it may be referred to as a pelt after initial treatment but before tanning, and is usually referred to as leather only after tanning has been carried out. For simplicity, however, in the present specification the word "leather" is used irrespectively of the stage within the overall treatment that has been reached. Thus, reference to a process for the production of leather need not itself result in a finished piece of leather, since for example a tanning process might follow; and reference to the treatment of leather does not imply that, for example, tanning has already been carried out. It may also be noted that the term leather does not imply the hide of any particular animal, although the invention will perhaps find greatest use in connection with bovine, caprine and ovine hides or skins.

The process of turning animal hides into commercial leather is, therefore, carried out by a series of processes which include not only the application of tanning agents but also the application of variety of other leather treatment agents.

The purpose of these processes is firstly to bring about an irreversible stabilization of hide that is otherwise prone to putrefaction, and secondly to impart desirable properties.

Hides usually arrive in a tannery in a temporarily cured state, usually brought about by packing in salt or by chilling. The first process in the tannery is then to soak the cured hides in clean water to remove salt, blood, dung and other dirt. Soaking also ensures complete rehydration of the hides in preparation for fleshing. The soaked hide is then passed through a fleshing machine which mechanically removes flesh or fat deposits from the flesh side of the hide, thereby facilitating chemical treatment in subsequent processes.

In order to remove hair, epidermis and residual inter-fibrillary components from the hide it is soaked for a period of from, say, 14 to 24 hours in a solution containing lime and sodium sulphide or other appropriate materials. This step of liming also serves to open up the fibre structure of the hide.

The hide is then de-limed by soaking in a weak acid solution of, for example, ammonium sulphate and ammonium chloride. This solution reacts with mechanically or chemically bound lime to form water-soluble salts, which can then be washed from the hide to remove the lime. Most types of hide are simultaneously treated with a bating material consisting of enzymes, usually pancreatic enzymes, which are used to remove residual components broken down by the lime. The bating material has the added benefit of giving a smoother grain and rendering the hide soft and flexible.

After de-liming and bating, the hides are washed in water several times to prepare them for pickling. The purpose of pickling is to acidify the hides to a certain pH, prior to tanning. Tanning may be effected using metal salts, usually chromium salts, but aluminum or zirconium salts or mixtures thereof may be used. Alternatively, the hides may be pre-tanned after the pickling stage, using for example modified aldehydes such as glutaraldehyde and modified glutaraldehyde.

As an alternative to the mineral tanning agents referred to above, natural vegetable tanning agents or synthetic organic tanning agents may be used.

Once the hide has been tanned or pre-tanned it has sufficient thermal and dimensional stability to allow various mechanical operations to be carried out. For example, the hide may be split through its thickness, and/or shaved.

Hides may then be processed further using, for example, chromium salts or other mineral tanning agents, vegetable extracts, synthetic tanning agents, polymeric materials, mixed tanning agents, dyes and fatliquors to impart, for example, specific properties such as colour, water-repellence and softness.

It may be noted here that dying is a very important part of leather processing, and it is frequently the most expensive single treatment. A variety of dyes may be used in the dying of leather, including acid dyes, direct dyes, solubilized sulphur dyes and reactive dyes. Common problems in leather dyeing include lack of uniformity and lack of penetration.

Fatliquoring too is an important process. In general, fatliquours include oils, fats, and waxes from natural or synthetic sources. These materials may be used in a raw or refined state. Furthermore, they may be processed by the addition of a surfactant or by chemical reactions such as sulfonation, chlorination, and phosphation to produce a material that is emulsifiable in water. Tanned leathers do not usually contain sufficient lubricants, and for this reason fatliquoring is carried out in order to produce the desirable softness and pliability. The process involves oils or other materials penetrating the collagen structure of the leather, ideally so that each fibre becomes uniformly coated. The result improves not only the handle and feel of the leather as mentioned above, but also extensibility, tensile and tear strength, hydrophilic and hydrophobic properties and permeability to water and air.

It can be seen therefore that leather production is a complex process which involves the application of a variety of chemical materials which in general must penetrate the collagen structure of the leather or at least become sufficiently well chemically and/or physically bound. Difficulties can frequently arise resulting in the need to apply to the leather greater quantities of the various leather treatment agents than are ultimately required in the finished product. Also, these agents frequently have to be employed at high concentrations, for long periods of time, and under particular processing conditions, such as high temperature, specific pH ranges and under particular mechanical conditions involving pressure or mechanical agitation.

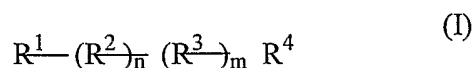
These disadvantages can result in added expense due to the increased amounts of chemical materials required and due to processing power requirements.

They can also result in environmental problems in removing and disposing of the necessary excess of the treatment agents that are not permanently incorporated into the leather.

We have now devised a way of overcoming these problems which involves applying to the leather a particular chemical material which appears to render the leather more receptive to the various chemical treatment agents required and which also appears to result in an enhanced effect relative to the amount of treatment agent employed on the leather. In some circumstances these beneficial effects can be achieved by treating the leather with the new chemical material and then removing that material before the usual leather treatment agent is applied. In this way, the new material may be recycled.

Whilst we do not wish to be bound by the theory, we believe that the new chemical material causes swelling of collagen of the leather by disrupting hydrogen bonds between collagen chains, and/or by increasing the effective number of binding sites for leather treatment agents.

Thus, the invention provides for the use of a material of formula (I) in the production of leather:



in which:

R^1 represents a substituted or unsubstituted group having a C8 to C18 (preferably C10 to C16) backbone;

R^2 represents an NHCO group;

R^3 represents a substituted or unsubstituted group having a C2 to C8 backbone;

R^4 represents an amine oxide, sulphonate, phosphate or betaine group;

n is 0 or 1; and

m is 0 or 1.

In particular, we have found that materials of formula (I) allow improved penetration or other application of a variety of leather treatment agents, for example:

- pretanning agents,
- tanning agents,
- retanning agents,
- lubricants,
- filling agents,
- softening agents,
- fatliquors,
- liming agents,
- de-liming agents,
- bating agents,
- dyes (particularly acid dyes), and
- dye fixing agents.

This improved application can result in faster processing for a given desired effect. We have noticed that the rate of uptake of certain leather treatment agents, particularly dyes, especially acid dyes, can be significantly increased. This effect is generally noted when the amount of the new material is at least 1% by weight based on the weight of the leather in its wet blue or other appropriate state. Also, it can result in a greater effect for a given offer of treatment agent. As mentioned above, it also appears that at least in some circumstances a greater effect is realised for a given quantity of treatment agent retained in the leather after the treatment step. Additional effects that can be achieved, particularly in connection with dyes, include colour enhancement, greater uniformity of effect over the surface of the leather, and more consistent penetration into the leather. As a result, the invention can lead not only to more economical and more environmentally friendly processing, but also to a more aesthetically pleasing and commercially valuable product.

Certain materials within the scope of formula (I) are known *per se*, although it has not been suggested that they be used in connection with leather; and it has not been suggested that they could provide the present benefits in connection with

treatments analogous to those referred to above when applied to other substrates. In general, it appears that the known compounds have been used as foam-boosting materials for use with shampoos, bleaches and detergents etc. and in combination with hair dyes.

Reference may be made to Dyes and Pigments, vol. 29, No. 1, pp23-44, 1995, The Characterisation of Treated and Dyed Hair by Guthrie et al. That paper discloses a material marketed by Huntsman Corporation, USA, under the trade mark Empigen OB. This material is described as a surfactant based on a mixture of n-lauryl- and myristyl- dimethylamine oxide. The material was used as part of a study undertaken to evaluate some of the factors that influence the dying of hair. Of course, hair is a fundamentally different material from leather, being based on keratin rather than on collagen.

US 5,948,124 discloses a composition for dying of human hair, and a large number of trade products is listed. One of these products is referred to by the trade mark Empigen. These products are disclosed for use in connection with basic dyes.

US 4,943,430 discloses a composition for use in the treatment of keratinous fibres, which materials include a cationic polymer, an anionic monomer and solubilizing agent chosen from amphoteric detergent active compounds, inorganic electrolytes and mixtures thereof.

US 5,914,445 discloses a preparation for dying wool which includes an amine oxide.

US 6,022,381 discloses compositions for colouring hair, wool, fur and other melanin containing fibres. The compositions may contain surfactants, and the particular Empigen disclosed is mentioned as a possible amphoteric surfactant.

US 6,004,355 also discloses the use of material marketed under the trade mark Empigen as a possible amphoteric surfactant for hair colouring compositions.

Certain compounds marketed under the trade mark Empigen by Huntsman Corporation may in fact be used as the present materials of formula (I). We have found that compounds marketed under the following specific trade marks are particularly useful: Empigen OB, Empigen OC/B, Empigen BB, Empigen AB/E, Empilan KCA. Also useful are materials marketed by Manro Limited of Cheshire,

England under the trade marks Manro AO30C and Manro BES 27. A further useful material is N-methylmorpholine-N-oxide.

At present we prefer those compounds marketed under the trade mark Empigen OB. These compounds are believed to correspond to materials of formula (I), where n is 0 and m is 0. In fact, in general we prefer that n be 0 and m be 0.

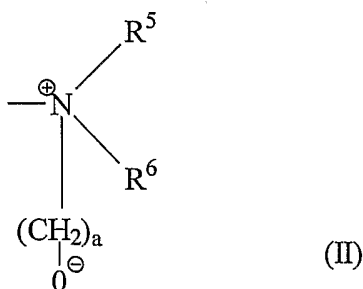
Also, we prefer that R¹ be unsubstituted or, if substituted be saturated and substituted with four or fewer groups, each of which has four or fewer carbon atoms. In general, we prefer that R¹ be non-polar or substantially non-polar, and preferably that it be an alkyl group. More preferably, R¹ has a C6 to C16 straight alkyl chain.

In general, it is preferred that the tail of the molecule of formula (I) be substantially linear and saturated, and also that it be substantially non-polar. Its length is preferably restricted in order that the overall molecule be soluble in water or aqueous solutions. In this way, the material may be applied to the leather in an aqueous solution, and because of the substantial linearity and non-polarity of the tail it can penetrate between collagen chains of the leather.

Certain materials other than those of formula (I) may also be used in the production of leather. Thus, the invention also provides for use of a substantially linear surfactant having an amphoteric head group in the production of leather, particularly for the incorporation into or onto the leather of one or more leather treatment agents such as those referred to above.

Group R⁴, the head group of the material of formula (I), is indeed preferably amphoteric at least under certain pH conditions such as from pH 7 to 9.

In particular, I prefer that R⁴ is a group of formula (II):



in which each of R⁵ and R⁶, which may be the same or different, is a straight or branched alkyl group having from 1 to 4 carbon atoms, and a is 0 or 1.

As mentioned above, the present invention is of particular use in connection with the dyeing of leather. The invention allows for an increase in the colour yield of the dye relative to the amount of dye applied to the leather and/or relative to the dyeing time. The invention may be used in connection with various dyes including acid dyes, direct dyes, solubilized sulphur dyes and/or reactive dyes. Dyes that may be used include those known as Acid Blue 612, Acid Red 97 and Acid Black 210.

The material provided by the invention may be applied to the leather prior to, and/or simultaneously with and/or after application of the appropriate leather treatment agent. Where it is applied prior to the leather treatment agent, the material, or at least some of it, may be removed prior to application of the leather treatment agent and optionally recycled. We believe that the effect of the new material may be permanent, or at least last long enough for a subsequent leather treatment process to benefit from its prior application. Where the new material and the leather treatment agent are applied simultaneously, they may be merely added to a suitable treatment vessel simultaneously, or they may be pre-mixed with one another and optionally with one or more additional materials to produce a new leather treatment composition.

Thus, the present invention additionally provides a composition for use in the production of leather, which comprises:

- (1) a material of formula (I) or a substantially linear surfactant having an amphoteric head group (which two possibilities are not of course mutually exclusive); and
- (2) one or more leather treatment agents, such as those referred to above.

Such a composition preferably comprises 0.1 to 10% by weight of component (1) and 0.1 to 30% by weight of any individual component (2).

The material provided by the invention, or a composition including it, may be applied to the leather by any suitable technique for example:

hand or machine padding,

roller coating,
curtain coating,
through feed roller application (sometimes known as padding in the textile industry),
drumming,
spraying, or
dip coating.

The material provided by the present invention may be used in conjunction with one or more additional materials such as a UV absorber, which may be applied to the leather before, simultaneously with or after application to the leather of the material in question. Such a UV absorber may form part of the composition referred to above.

The invention still further provides a material of formula (I) or a substantially linear surfactant having an amphoteric head group for use in the production of leather.

The invention yet further provides leather produced by the methods of the invention as well as articles comprising such leather. Examples of such articles include balls, articles of footwear, gloves or mitts, articles of clothing and leather goods. The term "leather goods" includes, for example, bags, saddlery, belts, watch straps, wallets, household goods, internal decoration or ornaments such as vases and bowls and sculptures, wall and floor coverings, bins and other containers, and industrial goods, such as a seals and bellows as well as furniture (both upholstery and structural).

The amount of new material used is preferably from 0.03% to 30% by weight based on the weight of the leather prior to the treatment in question. Preferably the amount is at least 0.1%, and more usually about 0.3%. The maximum will usually be considerably less than 30%, generally less than 10% and more usually less than 1%. Commercially available formulations might contain less than 100% of the desired active component. For example, the Empigen OB material referred to above is believed to contain about 30% by weight of the active component of present interest.

The pH at which application of the material takes place will depend on the nature of the leather treatment agent whose application is to be facilitated by the new material. However, it may be desirable to select a pH at which the amphoteric head group of the material is protonated at least following dye penetration, and possibly only following dye penetration. For many purposes a pH of less than 7 will be selected. Consideration must also be given to the level of washing to be employed and of the precise nature of the new material. A further consideration is the temperature at which the application is carried out, and for most purposes we prefer a temperature from 15 to 65°C, more usually 25°C to 50°C.

As mentioned above, the new material may be applied to the leather by various techniques, in particular by exhaustion from a liquor or by a dip coating technique employing rollers. This process is often referred to in the textile industry as padding. This term is also used in the leather industry for an alternative, acceptable, process by which a material is applied to the surface of the leather by contacting and rubbing over the surface with an absorbent structure carrying the material in question. Where the material is to be applied by exhaustion from liquor the leather will in general be immersed in a bath or other vessel which is raised to a desired treatment temperature for an appropriate period for time. This technique would include drumming in which a drum containing the leather and the material to be impregnated is rotated or otherwise agitated in order to enhance impregnation.

Although we do not wish to be bound by theory, we believe that the following provides an explanation of the mechanism underlying the invention. The end group R¹ of the new material is thought to penetrate the leather structure due to its linear nature; and a result of this penetration it acts to disrupt hydrogen bonding between adjacent collagen polypeptide helical chains of the leather. This may result in a degree of swelling of the fibrous material of the leather. Preferably, group R¹ is at least substantially non-polar and hydrophobic and these properties will facilitate penetration. We believe therefore that the greatest level of penetration of the new material will be achieved when the charge density of the leather is at a relatively low level. Furthermore, it appears that interaction between the leather and the head group R⁴ (or the amphoteric head group in the case of molecules not corresponding to

formula (I)) may occur under certain conditions as a result of the formation of hydrogen bonds. Under suitable circumstances the material will therefore become either chemically and/or physically bound to the leather as a result of penetration of the tail of the molecule and/or interaction with the head of the molecule. There is evidence that the mode of interaction between the new material and the leather is yet more complex, since interaction appears in some cases to be mediated by the presence of a dye or other leather treatment agent. For example, we have noticed that washing in water can, in some circumstances, remove some of the new material, but rarely that which is linked to applied dyestuffs.

Attention may also be drawn to the charge present on the head of the new molecule. Preferred materials that are believed to be amphoteric at a pH from 7.0 to 9.0 possibly become protonated at a pH of, say, 5.0 to 5.4. The presence of such protonated material in the leather structure appears to result in the generation of numerous additional effective sites for interaction with a dye. As a result, the potential number of dye molecules per unit area of the leather is increased and this appears to result in a greater concentration of colour or depth of shade.

We have noticed that if the new material is employed in sufficient concentration, then surface layers of the new material become established on the leather. This may result in a great increase of the depth of shade produced by a given quantity of dye. In some circumstances that may be desirable, but it can result in reduced penetration of the dye throughout the thickness of the leather. In such a circumstance we recommend that a reduced concentration of the material be employed to achieve a balance between depth of shade and penetration. An alternative approach is to employ a multi-stage dying process in which reduced concentrations of the new material and of the dye are used, followed by later additions of sufficiently high concentrations of the new material (and if necessary more dye) to establish surface layers on the leather at an appropriate part of the process. In a yet further alternative approach we employ a higher pH when the dye is applied. This allows the new material to remain non-ionic, prior to subsequent lowering of the pH which then encourages dye penetration. This may result from the Empigen or other material becoming cationic as a result of such treatment, giving

rise to an interaction between itself and the dye. In this way excellent depth of shade may be achieved together with good fixation of dye throughout the thickness of the leather.

Similar considerations to those set out above apply to the application of other leather treatment agents, such as fatliquor materials. Thus, good penetration and uniform lubrication of the fibre structure can be achieved. This results in more desirable and commercially valuable leather having uniform and repeatable characteristics.

Various leather treatment agents relevant to the present invention have been described above in general terms. Some more specific information may now be given. Tanning agents with which the invention has been found to be useful include poly(base)mineral tanning agents, poly(acid)mineral tanning agents, pyrogallol vegetable tanning agents, condensable catechol vegetable tanning agents, phenolic synthetic tanning agents, non-phenolic synthetic tanning agents, poly(condensation) and polymerisation compound tanning agents, paraffin derivative and fat-based aliphatic tanning agents, aliphatic aldehyde tanning agents, natural and synthetic oils, fats and waxes, and hydroxy alkyl phosphine tanning agents, for example of formula $[\text{HORPR}'_n\text{O}_m]_x\text{X}_y$ wherein R is an alkyl or alkenyl group having from 1 to 24 carbon atoms, R' is the same R or is an alkoxy group, X is an anion such that the compound is at least sparingly soluble in water, x is the valency of X, n is 2 or 3, m is 0 or 1, such that (n + m) is 2 or 3, and y is 0 or 1 such that (n + y) is 2 or 4. Also included are at least sparingly soluble condensates of any of the aforementioned compounds. The present invention may be used in connection with various fatliquoring agents, such as those comprising natural and synthetic oils, fats and waxes.

The dyes with which the invention may be used include nitro/nitroso dyes, metallized/non-metallized monoazo dyes, metallized/non-metallized polyazo dyes, stilbene dyes, di/triphenyl methane dyes, quinonimene dyes, oxazine dyes, thiazine dyes, azine dyes, sulphur dyes, pyridine/quinoline/acridine dyes, phthalocyanine dyes, indigoide/indigosoles dyes, anthraquinone/multi-ring dyes and natural dyes.

The Examples

The present invention is further illustrated by the following examples.

In the Examples of the invention the following materials of formula (I) above were used to aid the incorporation into leather of various dyes:

Empigen OB (believed to contain about 30% active material)

Empigen OC/B (believed to contain about 30% active material)

Empigen BB (believed to contain about 30% active material)

Empigen OS/A (believed to contain about 30% active material)

Empigen AB/E (believed to contain between 30 - 100% active material)

Empilan KCA (believed to contain between 30 - 100% active material)

Manro AO 30C (believed to contain about 30% active material)

N-methylmorpholine-N-oxide (believed to be supplied as a 50% active material)

and Manro BES 27(believed to contain about 30% active material).

These Empigen, Empilan and Manro names are trade marks, and the materials are obtainable from Huntsman Corporation and Manro Performance Chemicals Limited. N-methylmorpholine-N-oxide is obtainable from Huntsman Corporation. The Comparative Examples below are controls where the dye is applied to the leather in the absence of a material of formula (I).

The terms "offer" and quoted percentages of material are by reference to the wet blue weight at the start of processing.

The term "matched pair side" refers to a single hide that has been tanned and then divided into two halves. Matched pair sides were used in order to ensure fair comparisons between the examples of the invention and comparative examples.

All spectroscopic measurements were performed using a spectrometer marketed under the trade mark Datacolour Spectraflash SF300. The term K/S refers to the ratio of the Kubelka Munk constants, K (coefficient of absorption), and S (coefficient of scattering) which provides a relative measurement of colour strength or depth of shade.

All trials were carried out in a conventional stainless steel drum, run at a speed of 15 rpm.

Example 1 and Comparative Example 1

Matched sides were washed in 200% water and 2% formic acid (10%) at 35 °C for 20 minutes. After draining, the leather was neutralised with 1% sodium formate and 2.5% neutralising syntan in 100% water at 35 °C for 90 minutes. Process liquor pH was then in the range pH 4 – 5, and the cross-section of the leather was blue when tested with bromocresol green.

The drum was drained and leather washed in 200% water at 40 °C for 10 minutes.

After draining, the leather was run in 3% of an acrylic resin, 2% of a sulphited fish oil and 125% water at 40 °C. After 30 min, 5% of a vegetable tanning agent, 1% of a phenolic syntan, 3% of a cresylic syntan and 0.5 % sodium formate was added. After a further 60 minutes, the drum was drained and the leather washed for 10 minutes in 200% water at 40 °C.

After draining, the leather was run in 2% of a naphthalene sulphonic acid syntan, 0.5% ammonia and 50% water at 20 °C for 20 minutes.

1% of the dyestuff Acid Blue 612 and 1% Empigen OB was then added. After 210 minutes, a further 3% of a sulphited fish oil, 0.25% of a sulphochlorinated fish oil, 4% of a synthetic fatliquor and 25% water at 60°C was added and run for 60 minutes.

6% of formic acid (10%) was added and run for 30 minutes followed by a further 6% for a further 30 minutes. At this stage the process liquor pH was in the range pH 3.3 – 3.8.

The drum was then drained and the leather washed in 200% water at 30 °C for 10 minutes.

After draining, the leather was run in 0.6% sodium formate in 200% water at 30°C for 15 minutes.

On completion, the drum was drained and the leather removed and dried to a moisture content of 12 – 14%.

A plot of K/S obtained from the UV-visible absorbance spectrum for this leather gave an integral value of 11.9.

In Comparative example 1, the process detailed above was repeated but with the omission of Empigen OB. A similar plot of K/S from this leather gave an integral value of 5.4.

By relating K/S to depth of shade, one can see that the leather sides treated with Empigen OB show an improvement in depth of shade of 121% relative to the leather sides not treated with Empigen OB.

Example 2

The procedure of Example 1 was repeated, but instead of using the dye preparation:

1.0% Acid Blue 612

1.0% Empigen OB

using,

0.5% Acid Blue 612

1.0% Empigen OB

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 5.75. A repeat of this wet processing procedure was performed with the omission of Empigen OB. A resultant plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 5.8.

By relating K/S to intensity of colour, one can see that the leather sides treated with Empigen OB show a difference in colour strength of 1% on the use of a 50% reduction in dye offer.

Example 3

The procedure of Example 1 was repeated, but instead of using the dye preparation:

1.0% Acid Blue 612

1.0% Empigen OB

using,

1.0 % Acid Red 97

0.5% Empigen OB

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides produced gave an integral value of 16.6. The procedure of Example 1 was also repeated with the following dye preparation.

1.0 % Acid Red 97

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides produced an integral value of 10.7.

By relating K/S to intensity of colour, one can see that the leather sides treated with Empigen OB show an improvement in colour strength of 56% relative to the leather sides not treated with Empigen OB.

Example 4 and Comparative Example 2

The procedure of Example 1 was repeated, but instead of using the dye preparation:

1.0% Acid Blue 612

1.0% Empigen OB

using,

1.0% Acid Red 97

2.0% Empigen OB

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides produced gave an integral value of 19.2.

In Comparative Example 2 the procedure of Example 1 was repeated, but with the following dye preparation:

1.0% Acid Red 97.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides produced an integral value of 10.7.

By relating K/S to intensity of colour, one can see that the leather sides treated with Empigen OB show an improvement in colour strength of 79% relative to the leather sides not treated with Empigen OB.

Example 5 and Comparative Example 3

Matched sides were washed in 300% water at 35 °C for 20 minutes. After draining, the leather was run in 2.5% sodium formate and 150% water at 35 °C for 30 minutes. 1.5% sodium bicarbonate was then added. After 270 minutes the process liquor pH was in the range pH 4.8 – 5.8 and the cross-section of the leather was blue when tested with bromocresol green.

After draining, the leather was washed twice with 200% water at 35 °C for 10 minutes. After the second drain, the leather was run in 0.2% of a polymeric dispersing agent, 2% of a silicone based fatliquor and 50% of water at 35 °C. After 10 minutes, 3% of an acrylic resin and 25% water at 45 °C was added. After a further 20 minutes, 1% of a phenolic syntan was added. After a further 10 minutes, 3% of a melamine syntan was added. After a further 20 minutes, 4% of a vegetable tanning agent was added. After a further 60 minutes, 1% of the dyestuff Acid Black 210, 1% Empigen OB and 25% water at 40 °C was added.

After 90 minutes, the temperature of the process liquor was raised to 50 °C over a period of 20 minutes. 0.5% of a polymeric dispersing agent, 6% of a silicone-based fatliquor and 100% water at 50 °C were then added and run for 90 minutes.

6% formic acid (10%) was added and run for 30 minutes followed by another 6% formic acid (10%) for a further 15 minutes. At this stage the process liquor pH was in the range pH 3 – 3.8.

The leather was then washed for 10 minutes in 200% water at 30 °C. After draining, 3% chromium sulphate (30%) and 50% water at 30 °C was added. After 90 minutes, 50% water at 50 °C was added and run for a further 30 minutes. After draining, the leather was washed with 200% water at 25 °C.

On completion, the drum was drained and the leather removed and dried to a moisture content of 12 – 14%.

A plot of K/S obtained from the UV-visible absorbance spectrum for this leather gave an integral value of 54.1.

In Comparative example 3, the process detailed above was repeated but with the omission of Empigen OB. A similar plot of K/S from this leather gave an integral value of 20.7.

By relating K/S to depth of shade, one can see that the leather sides treated with Empigen OB show an improvement in depth of shade of 161% relative to the leather sides not treated with Empigen OB.

Example 6

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0 % Empigen OB

using,

1.0 % Acid Black 210

1.0 % Empigen OC/B.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 27.9.

By relating K/S to intensity of colour, one can see that the leather side treated with Empigen OC/B shows an improvement in colour strength of 97% relative to the control of Comparative Example 3. This figure was calculated from comparisons firstly between the effect of Empigen OC/B and that of Empigen OB, and secondly between the effect of Empigen OB and the control of Comparative Example 3.

Example 7

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0 % Empigen OB,

using,

1.0 % Acid Black 210

1.0 % Empigen BB.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 17.1.

By relating K/S to intensity of colour, one can see that the leather sides treated with Empigen BB show an improvement in colour strength of 25% relative to the control of Comparative Example 3. A calculation was used analogous to that used in Example 6.

Example 8

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0 % Empigen OB,

using,

1.0 % Acid Black 210

1.0 % Empigen AB/E.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 18.9.

By relating K/S to intensity of colour, one can see that the leather sides treated with Empigen OC/B show an improvement in colour strength of 27% relative to the control of Comparative Example 3. A calculation was used that was analogous to that used in Example 6.

Example 9

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0 % Empigen OB,

using

1.0 % Acid Black 210

1.0 % Empilan KCA3.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value 22.0.

By relating K/S to intensity of colour, one can see that the leather sides treated with Empigen KCA3 show an improvement in colour strength of 48% relative to the control of Comparative Example 3. A calculation was used that was analogous to that used in Example 6.

Example 10

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0% Empigen OB,

using,

1.0% Acid Black 210

1.0% Manro AO30C.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 23.5.

By relating K/S to intensity of colour, one can see that the leather sides treated with Manro A030C show an improvement in colour strength of 61% relative to the control of Comparative Example 3. A calculation was used that was analogous to that used in Example 6.

Example 11

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0 % Empigen OB

using,

1.0 % Acid Black 210

1.0 % N-methylmorpholine-N-oxide.

A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 21.0.

By relating K/S to intensity of colour, one can see that the leather sides treated with N-methylmorpholine-N-oxide show an improvement in colour strength of 42% relative to the control of Comparative Example 3. A calculation was used that was analogous to that used in Example 6.

Example 12

The procedure of Example 5 was repeated, but instead of using the dye preparation:

1.0 % Acid Black 210

1.0 % Empigen OB,

using,

1.0 % Acid Black 210

1.0 % Manro BES27.

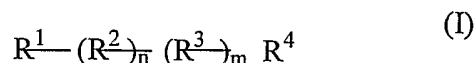
A plot of K/S from the UV-visible absorbance spectrum of the resultant leather sides gave an integral value of 16.3.

By relating K/S to intensity of colour, one can see that the leather sides treated with Manro BES27 show an improvement in colour strength of 16% relative to the control of Comparative Example 3. A calculation was used that was analogous to that used in Example 6.

EXAMPLE	MATERIAL	COLOUR STRENGTH
Comparative 3	Std	100
5	Empigen OB	261
6	Empigen OC/B	197
7	Empigen BB	125
8	Empigen AB/E	127
9	Empilan KCA 3	148
10	Manro AO30C	161
11	N-Methylmorpholine-n-oxide	142
12	Manro BES 27	116

CLAIMS

1. Use of a material of formula (I) in the production of leather:



in which:

R^1 represents a substituted or unsubstituted group having a C8 to C18 backbone;

R^2 represents a NHCO group;

R^3 represents a substituted or unsubstituted group having a C2 to C8 backbone;

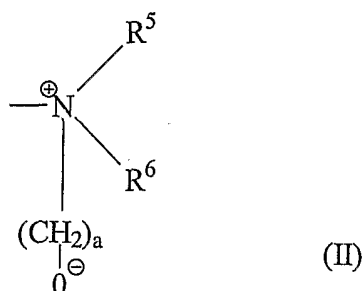
R^4 represents an amine oxide, sulphonate, phosphate or betaine group;

n is 0 or 1; and

m is 0 or 1.

2. Use according to claim 1, in which n is 0 and m is 0.
3. Use according to claim 1 or 2, in which R^1 is unsubstituted or is saturated and substituted with four or fewer groups each of which has four or fewer carbon atoms.
4. Use according to any of claims 1,2 and 3, in which R^1 is non-polar.
5. Use according to any preceding claims, in which R^1 is an alkyl group.
6. Use according to any preceding claim, in which R^4 is amphoteric.
7. Use according to any preceding claim, in which R^4 is a group of formula (II):

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in which each of R^5 and R^6 , which may be the same or different, is a straight or branched alkyl group having from 1 to 4 carbon atoms, and a is 0 or 1.

8. Use according to any preceding claim, for the incorporation into and/or onto the leather of one or more leather treatment agents.

9. Use according to claim 8, in which the leather treatment agent comprises:

- a pre-tanning agent,
- a tanning agent,
- a retanning agent,
- a lubricant,
- a filling agent,
- a softening agent,
- a fatliquor,
- a liming agent,
- a de-liming agent,
- a bating agent,
- a dye, or
- a dye fixing agent.

10. Use according to claim 9 for increasing the colour yield of a dye relative to the amount of dye applied to the leather and/or relative to the dying time.

11. Use according to claim 9 or 10, in which the treatment agent comprises an acid dye, a direct dye, a solubilized sulphur dye and/or a reactive dye.
12. Use according to any of claims 8 to 11, in which the material of formula (I) is applied to the leather prior to or simultaneously with the leather treatment agent.
13. Use according to claim 12, in which material of formula (I) is applied to the leather prior to the leather treatment agent; at least part of said material is then removed from the leather; and then said agent is applied to the leather.
14. Use according to any preceding claim, in which the material of formula (I) is applied to the leather by:
 - hand or machine padding,
 - roller coating,
 - curtain coating,
 - through feed roller application,
 - drumming,
 - spraying, or
 - dip coating.
15. Use according to any preceding claim in which a UV absorber is applied to the leather before, simultaneously with, or after application to the leather of the material of formula (I).
16. Use according to any preceding claim, in which the material of formula (I) serves to cause swelling of collagen of the leather by disrupting hydrogen bonds between collagen chains.
17. Use according to any preceding claim, in which the material of formula (I) serves to increase the effective number of binding sites for leather treatment agents.

18. A material of formula (I) as defined in any of claims 1 to 7 for use in the production of leather.
19. Use of a substantially linear surfactant having an amphoteric head group in the production of leather.
20. Use according to claim 19, for the incorporation into and/or onto the leather of one or more leather treatment agents.
21. Use according to claim 20, in which the leather treatment agent comprises:
- a pre-tanning agent,
 - a tanning agent,
 - a retanning agent,
 - a lubricant,
 - a filling agent,
 - a softening agent,
 - a fatliquor,
 - a liming agent,
 - a de-liming agent,
 - a bating agent,
 - a dye, or
 - a dye fixing agent.
22. Use according to any of claims 19, 20 or 21, for increasing the colour yield of a dye relative to the amount of dye applied to the leather and/or relative to the dying time.
23. Use according to any preceding claim, wherein the material of formula (I) or the surfactant as the case may be serves to cause swelling of collagen of the leather

by disrupting hydrogen bonds between collagen chains and/or to increase the effective number of binding sites for leather treatment agents.

24. A substantially linear surfactant having an amphoteric head group for use in the production of leather.

25. A composition for use in the production of leather, which comprises:

- (1) a material of formula (I) as defined in any of claims 1 to 7 or a substantially linear surfactant having an amphoteric head group; and
- (2) one or more leather treatment agents.

26. A composition according to claim 25, in which the leather treatment agent comprises:

- a pre-tanning agent,
- a tanning agent,
- a retanning agent,
- a lubricant,
- a filling agent,
- a softening agent,
- a fatliquor,
- a liming agent,
- a de-liming agent,
- a bating agent,
- a dye, or
- a dye fixing agent.

27. A composition according to claim 26, in which the agent comprises a dye.

28. A composition according to claim 27, which comprises 0.1 to 10% by weight of component (1) and 0.1 – 30% by weight of any individual component (2).

29. A composition according to any of claims 25 to 28, which additionally comprises:

(3) a UV-absorber.

30. Leather produced by a method that involves the use according to any of claims 1 to 17 and 19 to 23.

31. An article comprising leather according to claim 30.

32. An article according to claim 31, being:

a ball,

an article of footwear,

a glove or mitt,

an article of clothing, or

leather goods.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03413

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C14C9/00 D06P1/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C14C D06P		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	CH 638 649 A (SANDOZ AG) 14 October 1983 (1983-10-14)	19-21, 23-26, 30-32
A	page 3, right-hand column, line 12 -page 5, right-hand column, line 60 page 6, line 5 -page 8, right-hand column, line 14 claims 1,4-7	6,7
X	DATABASE WPI Section Ch, Week 199104 Derwent Publications Ltd., London, GB; Class D18, AN 1991-028168 XP002218840 & SU 1 546 496 A (LENIN STATE LIBRARY), 28 February 1990 (1990-02-28) abstract	1-5,8,9, 12,14, 16-18, 25,26, 30-32
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☒ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
30 October 2002		12/11/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Neugebauer, U

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/03413

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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