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(54) **Fabric conditioning article, method of manufacturing same, and method of conditioning clothes therewith.**

(57) An article useful for the conditioning of clothes in an laundry dryer during the drying cycle is produced which comprises a flexible polyurethane foam substrate impregnated with an effective amount of a conditioning agent and which has on at least one surface of the substrate a pattern which is substantially removed from the substrate during the drying cycle thereby indicating to the user of the article that the conditioning agent has been substantially removed from the article during the course of the drying cycle.

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Fabric Conditioning Article, method of manufacturing same, and method of conditioning clothes therewith

The present invention is concerned with an article useful for conditioning clothes in an laundry dryer during the drying cycle which article has a pattern thereon which is substantially removed from the article during the course of the drying cycle thereby indicating to the user of the article that the conditioning agent which the article contained has been substantially used up during the course of the drying cycle.

Various dryer added fabric conditioning agents for use in automatic laundry dryers for the purpose of conditioning clothes such as to provide softness and/or antistatic properties thereto or bacteriostatic or fungicidal properties thereto are known in the art. Such articles comprise a fibrous, woven or nonwoven flexible substrate coated or impregnated with a suitable fabric conditioning agent or a flexible polyurethane foam substrate impregnated with a suitable fabric conditioning agent which will transfer from the substrate to the clothes to be conditioned during the drying cycle in an automatic laundry dryer. Frequently the user of such an article will attempt to reuse the article on a subsequent

bundle of clothes and will be disappointed that the conditioning achieved from the first use is not repeated for the second.

The present invention provides a decorative pattern on the substrate which is visible to the user at the time the substrate is initially place in a laundry dryer with the clothes to be conditioned and which pattern substantially disappears from the substrate during the course of the drying cycle. The disappearance of the pattern is intended to indicate to the user that the conditioning agent has been substantially used up and that the substrate therefore does not contain a sufficient amount of conditioning agent to render the article useful a second or subsequent time. According to the present invention there is provided an article useful for conditioning clothes in a laundry dryer during the drying cycle which comprises a flexible polyurethane foam substrate impregnated with an effective amount of a conditioning agent and having on at least one surface of the substrate a pattern formed by an ink which adheres to the surface, is stable to the conditioning agent and is stable during the impregnation of the substrate with the conditioning agent, and which pattern substantially disappears from the substrate during this drying cycle. The conditioning agent comprises a fabric softening agent, an antistatic agent, a fabric softening and antistatic agent, a bacteriostatic or a fungicide.

The ink used to print the pattern on the substrate preferably comprises a titanium dioxide (TiO_2) water-based ink containing a suitable binder. The loading of ink, measured as dried ink, is preferably from 0.05 to 60 gm^{-2} within the patterned area. When the conditioning agent is a fabric softening and antistatic agent one

suitable class are cationic quaternary ammonium salts or a cationic quaternary ammonium salt in combination with a suitable nonionic sufactant. Any quaternary ammonium salt or combination of quaternary ammonium salt and/or suitable nonionic surfactant which salt, mixture of salts or mixture is known in the art to exhibit fabric softening and antistatic effect and which is compatible for impregnation into a flexible polyurethane foam substrate may be used.

Particularly useful cationic quaternary ammonium salts are: dodecyltrimethyl ammonium chloride;
didodecyldimethyl ammonium chloride;
tetradecyltrimethyl ammonium chloride;
ditetradecyldimethyl ammonium chloride;
pentadecyltrimethyl ammonium chloride;
dipentadecyldimethyl ammonium chloride;
didodecyldiethyl ammonium chloride;
didodecyldipropyl ammonium chloride;
ditetradecyldiethyl ammonium chloride;
ditetradecyldipropyl ammonium chloride;
ditallowdiethyl ammonium chloride;
ditallowdipropyl ammonium chloride;
tallowdimethyl benzyl ammonium chloride;
tallowdiethyl benzyl ammonium chloride;
dodecyltrimethyl ammonium methyl sulphate;
didodecyldiethyl ammonium acetate;
tallowtrimethyl ammonium acetate;
tallowdimethyl benzyl ammonium nitrite;
ditallowdipropyl ammonium phosphate;
tallowtrimethyl ammonium chloride;
tallowdimethyl (3-tallowalkoxpropyl) ammonium chloride;

ditallow dimethyl ammonium chloride;
ditallow dimethyl ammonium methyl sulphate;
icosyltrimethyl ammonium chloride;
di-icosyldimethyl ammonium chloride;
methyl-1-coco amido ethyl-2-coco imidazolinium methyl sulphate;
methyl-1-soya amido ethyl-2-soya imidazolinium methyl sulphate;
methyl-1-tallow amido ethyl-2-tallow imidazolinium methyl sulphate;
methyl-1-oleyl amido ethyl-2-oleyl imidazolinium methyl sulphate; and
methyl-1-tallow amido ethyl-2-tallow imidazolinium chloride.

Particularly suitable zwitterionic quaternary ammonium compounds are:

3-(N-icosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;
3-(N-icosyl-N,N-dimethylammonio)propane-1-sulphonate;
3-(N-icosyl-N,N-di(2-hydroxyethyl)ammonio)-2-hydroxypropane-1-sulphonate;
3-(N-docosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;
3-(N-docosyl-N,N-dimethylammonio)propane-1-sulphonate;
3-(N-docosyl-N,N-bis-(2-hydroxyethyl)ammonio)-2-hydroxypropane-1-sulphonate;
3-(N-tetracosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;
3-(N-tetracosyl-N,N-dimethylammonio)propane-1-sulphonate;

3-(N-tetracosyl-N,N-bis(2-hydroxyethyl)ammonio)-2-hydroxypropane-1-sulphonate;

3-(N-hexacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-hexacosyl-N,N-dimethylammonio)propane-1-sulphonate;

3-(N-icosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-docosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-tetracosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-henicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-tricosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-tricosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-tricosyl-N,N-dimethylammonio)propane-1-sulphonate;

3-(N-pentacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-(2-methoxydocosyl)-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-heptacosyl-N,N-dimethylammonio)propane-1-sulphonate;

3-(N-octacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-nonacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate;

3-(N-triacontyl-N,N-dimethylammonio)propane-1-sulphonate;

3-(N-(3,5-dioxatetracosyl)-N,N-dimethylammonio)-2-hydroxypropane-1-sulphonate.

Suitable anionic sulphonates include:

sodium or potassium 2-acetoxydocosylsulphonate;
ammonium 2-acetoxydocosylsulphonate;
diethanolammonium 2-acetoxydocosylsulphonate;
sodium or potassium 2-acetoxytricosyl sulphonate;
sodium or potassium 2-acetoxytetracosyl sulphonate;
sodium or potassium 2-acetoxypentacosyl sulphonate;
sodium or potassium 2-acetoxyhexacosyl sulphonate;
sodium or potassium 2-acetoxyheptacosyl sulphonate;
sodium or potassium 2-acetoxyoctacosyl sulphonate;
2-acetoxynonacostyl sulphonate;
2-acetoxytriacontyl sulphonate;
2-acetoxyhenitriacontyl sulphonate; and
2-acetoxydotriacontyl sulphonate.

Particularly suitable softening nonionics include:

β-hydroxydocosyldimethylphosphine oxide;
henicosylimethylethylphosphine oxide;
docosylmethylethylphosphine oxide;
tricosyldiethylphosphine oxide;
tricosyldimethylphosphine oxide;
tetracosyldi(2-hydroxyethyl)phosphine oxide;
pentacosyldimethylphosphine oxide;
icosylmethyl-2-hydroxybutylphosphine oxide;
icosyldibutylphosphine oxide;
docosylmethyl-3-hydroxybutylphosphine oxide;
hexacosyldiethylphosphine oxide;
heptacosyldimethylphosphine oxide;
octacosyldiethylphosphine oxide;
triacontyldimethylphosphine oxide;
icosyldimethylphosphine oxide;

icosyldi (2-hydroxyethyl)phosphine oxide;
docosyldimethylphosphine oxide;
docosyldi(2-hydroxyethyl)phosphine oxide;
tetracosyldimethylphosphine oxide;
hexacosyldimethylphosphine oxide;
icosyldiethylphosphine oxide;
docosyldiethylphosphine oxide;
tetracosyldi(2-hydroxyethyl)phosphine oxide;
icosylmethylethylphosphine oxide;
henicosyldimethylphosphine oxide;
β-hydroxyicosyldimethylphosphine oxide;
icosyl-bis(β-hydroxyethyl)amine oxide;
icosyldimethylamine oxide;
docosyldimethylamine oxide;
docosyl-bis(β-hdyroxyethyl)amine oxide;
tetracosyldimethylamine oxide;
tetracosyl-bis (β-hydroxyethyl)amine oxide;
hexacosyldimethylamine oxide;
hexacosyl-bis (β-hydroxyethyl)amine oxide;
2-hydroxyicosyldimethylamine oxide;
icosylmethylethylamine oxide;
icosyldiethylamine oxide;
2-hydroxyicosyldiethylamine oxide;
henicosyldimethylamine oxide;
henicosyldiethylamine oxide;
docosyldiethylamine oxide;
tricosyldimethylamine oxide;
tricosyldiethylamine oxide;
tetracosyldiethylamine oxide;
β-hydroxytetracosyldimethylamine oxide;
pentacosyldimethylamine oxide;
hexacosyldiethylamine oxide;
icosylmethyl (2-hydroxypropyl)amine oxide;

docosylbutylmethylamine oxide;
2-docosenyldimethylamine oxide;
2-methoxydocosyldimethylamine oxide;
heptacosyldimethylamine oxide;
octacosylmethylethylamine oxide;
octacosyldiethylamine oxide;
nonacosyldimethylamine oxide;
triacontyldiethylamine oxide;
3,6-dioxaoctacosyldimethylamine oxide;
2-hydroxy-4-oxatetracosyldimethylamine oxide;
6-stearamidohexyldimethylamine oxide;
glycerol-1-monolaurate;
glycerol-1-monomyristate;
glycerol-1-monopalmitate;
glycerol-1-monostearate;
glycerol-1-monobehenate;
glycerol-1-monlignicerate;
glycerol-1-monarachidoate;
glycerol-1,3-dipalmitate;
glycerol-1,3-distearate;
glycerol-1-palmitate-3-laurate;
glycerol-1-palmitate-3-stearate;
glycerol-1,3-dibehenate;
trilaurin;
trimyristin;
triolein;
tristearin;
-palmitodistearin;
β-stearopalmitolein;
β-palmitodistearin;
sobitan fatty acid esters (mentioned in U.S. Patent No. 4,022,938 (Zaki, et al)

In addition to the above mentioned nonionics which function as the main or auxiliary softening agents in the present invention, there is a second class of nonionics which are also useful as melting point depressants and transfer faciltators to the previously mentioned softening compounds (quaternary ammonium salts, anionic and nonionic). Particularly suitable classes of these compounds include the following:

polyoxyethylene fatty acid esters;
polyoxypropylene fatty acid esters;
polyoxyethylene fatty alcohol ethers.

When the conditioning agent is a quaternary ammonium salt it will have at least one of the properties of softening fabrics and conveying antistatic properties on to fabrics.

The present invention also includes a method of conditioning clothes in a laundry dryer during the drying cycle, which method comprises placing in the dryer the article according to the invention together with the clothes to be conditioned.

A further aspect of the present invention comprises a method for producing the article of the invention which comprises imprinting a desired pattern on a flexible polyurethane foam substrate either prior to impregnation of the polyurethane foam substrate with the conditioning agent or subsequent to the impregnation. The ink used to imprint the pattern must be one which adheres to the substrate, is stable to the conditioning agent and if the

pattern is applied prior to the impregnation step, the ink must be stable during the impregnation step and the ink must be such that the pattern substantially disappears from the substrate during the drying cycle of a laundry dryer. The fabric conditioning agent with which the polyurethane foam substrate is impregnated may comprise a fabric softening agent, an antistatic agent, a fabric softening and antistatic agent, a bacteriostatic agent or a funticide.

An ink which meets the above criteria is suitably a titanium dioxide water-based ink containing a suitable binder has been found to be particularly useful. The loading of ink measured as dried ink within the patterned area is preferably from 0.05 to 60 gm^{-2} of finished product.

When the conditioning agent is a fabric softening agent and antistatic agent, it is preferably a quaternary ammonium salt, a mixture of such salts or a quaternary ammonium salt in combination with a suitable nonionic surfactant. When the fabric conditioning agent with which the substrate is impregnated is a quaternary ammonium salt or mixture of such salts, said compounds will have at least one of the properties of softening fabrics and conveying antistatic properties thereto.

Suitable quaternary ammonium salts and nonionic surfactants have been described above.

The flexible polyurethane foam substrate which is preferred for use according to the present invention preferably has a thickness of approximately 0.22 cm and a density of approximately 24 Kg m^{-3}. It is preferably

an open-celled polyurethane foam and preferably the pore density is about 11 pores per cm^2. If desired, the substrate may be coloured to provide a contrast to the ink which is used to form the pattern.

While with what is described above any ink system which meets the above set forth criteria may be used, one particularly acceptable ink system is Aqualox II (registered Trade Mark), white, which is an ink system of Inmont Corporation. This ink consists of 35% TiO_2 in a water-base with an acrylic binder. Many inks contain binders or pigments which are readily dissolved into the active system of the substrate of dryer-added fabric softeners in conditioning agents and thus react with the substrate. This would result in problems during the impregnation of the substrate with the conditioning agent and would also be likely to cause staining of the clothes during the conditioning step in the dryer. Although the pattern substantially disappears from the substrate during the course of the drying cycle, the unique partial solvation of the binder by the active system both permits the transfer of conditioning agent and inhibits staining of the clothes.

The desired pattern may be imprinted under the flexible substrate by using any standard flexographic printing press. The flexographic printing press utilises a rotary flexible rubber plate in conjunction with a rapid drying ink. While the preferred loading of ink, measured as dry ink, within the patterned area as has been described above as being within the range of 0.05 to 60 g m^{-2}, the preferred loading range is in the range of 0.05 to 4.2 g m^{-2}.

The following Example illustrates the present invention.

Example

Aqualox II (registered Trade Mark), white, a TiO_2 water-based ink available commercially from Inmont Corp. Lodi, N.J., U.S.A. was used to print a roll of polyurethane foam. The open-celled polyurethane foam had a thickness of 0.22 cm, a density of 24 Kg m^{-3} and a pore density of 11 pores cm^{-2}. A flexographic printing unit, Model 45-6, manufactured by Wolverine Flexographic Presses, Farmington, Michigan, U.S.A., was used along with a 55 durometer synthetic rubber printing plate. The plate's raised printing surface consisted of 25% of the total surface area and individual designs were 1.48 cm^2 in area. The average dry ink loading onto the foam was 3.2 g m^{-2} within the printed areas, or approximately 0.8 g m^{-2} over the total surface of the foam.

The printed foam was then impregnated with a 5:3 mixture of dimethyl di-(hydrogenated-tallow)ammonium methylsulphate polyethoxylated glycol ester in a liquid state at 82°C. The impregnation process is accomplished via a pair of compression rollers neither of which showed any visible evidence of ink solids either during or after the run.

The finished printed and impregnated foam was then cut into 7.6 x 17.8 cm sheets and evaluated in a standard residential clothes dryer. After a normal 50 minute drying cycle the pattern had substantially disappeared leaving no trace of any visible residue on the dark synthetic item used in the testing bundle.

CLAIMS

1. An article useful in conditioning clothes in a laundry dryer during the drying cycle, which comprises a flexible polyurethane foam substrate impregnated with an effective amount of a conditioning agent and having on at least one surface of the substrate a pattern formed by an ink which adheres to the substrate, is stable to the conditioning agent and is stable during the impregnation of the substrate with the conditioning agent, and which pattern substantially disappears from the substrate during the drying cycle.

2. An article according to claim 1, characterised in that the conditioning agent comprises a bacteriostatic agent, a fungicide, a fabric softening agent, an antistatic agent, or a combined fabric softening and antistatic agent.

3. An article according to claim 2, characterised in that the conditioning agent comprises a cationic fabric softening and antistatic agent.

4. An article according to claim 2, characterised in that the fabric softening and antistatic agent comprises a quaternary ammonium salt alone or in combination with a suitable nonionic surfactant.

5. An article according to any one of claims 1 to 4, characterised in that the ink comprises a TiO_2 water-based ink containing a suitable binder.

6. An article according to any one of claims 1 to 5, characterised in that the loading of ink, measured as dried ink, is from 0.05 to 60 g m^{-2} within the patterned area.

7. A method of conditioning clothes in a laundry dryer during the drying cycle, which method comprises placing in the dryer an article according to any one of claims 1 to 6, together with the clothes to be conditioned.

8. A method of producing an article according to any one of claims 1 to 6, which method comprises imprinting a desired pattern on a flexible polyurethane foam substrate with an ink which adheres to the substrate and which substantially disappears from the substrate during the drying cycle, and impregnating the substrate with an effective amount of fabric conditioning agent or agents, the ink being stable to the conditioning agent.

9. A method of producing an article according to any one of claims 1 to 6, which method comprises impregnating a polyurethane foam substrate with an effective amount of a fabric conditioning agent or agents, and thereafter printing on the substrate a pattern with an ink which adheres to the impregnated substrate, is stable to the conditioning agent and substantially disappears during the drying cycle of a laundry dryer.

10. A tablet as claimed in claim 1 and substantially as hereinbefore described with reference to the Example.

11. A method of conditioning clothes as claimed in claim 7 and substantially as hereinbefore described with reference to the Example.

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European Patent Office

Application number
EP 81 30 5303

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	GB - A - 2 007 096 (EXTERMA-GERM. PRODUCTS) * Whole document *	1,2
A	US - A - 3 118 060 (E. KLEIN)	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 11 D 17/04
D 06 M 16/00
D 06 M 13/46

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 11 D 17/04
3/48
3/40
3/00
D 06 M 16/00
D 06 F 58/20

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	19-01-1982	GOLLER