

[54] ANTISTATICALLY PROTECTED
NONWOVEN POLYOLEFIN SHEET

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[22] Filed: Feb. 29, 1972

[21] Appl. No.: 230,448

[52] U.S. Cl.117/135.5, 117/138.8 E,
117/139.5 CQ

[51] Int. Cl. C09d 3/00

[58] Field of Search117/138.8 E, 135.5,
117/139.5 CQ

[56] References Cited

UNITED STATES PATENTS

2,413,428 12/1946 Billings 117/139.5 X
3,169,899 2/1965 Steuber 156/62.2 X

3,442,740 5/1969 David..... 156/181
3,478,141 11/1969 Dempsey et al. 156/166 X
3,658,573 4/1972 Guestaux et al. 117/138.8 X
3,703,588 11/1972 Saito et al. 117/138.8 X

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[57] ABSTRACT

Nonwoven sheets comprised of film-fibril elements of an olefin polymer and bearing at least 0.1 percent by weight, preferably 0.3 to 0.4 percent by weight of a non-rewettable finish defined by the formula: $M_nR_{3-n}PO_4$ where M is selected from the group consisting of lithium, sodium, potassium, and ammonium ions, R represents an alkyl group containing 3 to 5 carbon atoms, and n is selected from the integers 1 and 2.

4 Claims, No Drawings

ANTISTATICALLY PROTECTED NONWOVEN POLYOLEFIN SHEET

BACKGROUND OF THE INVENTION

Methods are available for preparing nonwoven polyolefin sheets which exhibit the ability to function as a barrier to liquid water while still permitting passage of water vapor, by fibrillating an oriented polymeric film to form a network and then laminating together several layers with fibrils oriented in different directions in the various layers. In one method, a solution of polymer is flash-spun at a temperature above the boiling point of the solvent and at a high pressure into a low pressure area, whereupon a three-dimensional network of film-fibrils forms at the spinneret. The network is spread by means of a baffle and is then collected in multidirectional, overlapping, and intersecting arrangement on a moving belt. The sheet may be consolidated by passing it through the nip of a pair of cold rolls. A hot embossing process for improving the delamination and abrasion resistance of such sheets while retaining the softenableity of the sheet is also known. Such nonwoven products exhibit desirable combinations of softness, drape, breatheability, etc., which has led to their acceptance for use in disposable or limited-use garments, as protective wrapping materials, drapes and curtains, etc.

The ability to function as a barrier to liquid water while still permitting passage of water vapor results from the film-fibril structure of the nonwoven sheet which permits passage of water (and other gaseous) vapor through the tortuous paths from one surface of the sheet to the opposite surface provided by the microscopic channels between the relatively close packed film-fibril elements, while liquid water is precluded from penetrating these same channels due to their small size and the hydrophobic character of the polyolefin polymer surface. The relative freedom for passage of vapor through the nonwoven sheets can be varied over a substantial range, depending on how tightly compacted (how highly calendered or embossed) the sheets may be, whether subsequent to bonding or embossing the sheet has been mechanically worked to loosen up the film-fibril structure between bond points, and on the total basis weight of the sheet etc. In any event, the water barrier property continues to be exhibited, provided the nonwoven sheet remains free from gross holes as might be deliberately introduced.

Such nonwoven fibrous sheets having vapor transmission and liquid water barrier properties have obvious potential utility in a multitude of applications, e.g., disposable, protective garments such as surgeon's gowns; protective wrap for various commodities such as carpets, fiber bales, lumber, grain, etc.; sterile packaging permeable to sterilizing gases but impermeable to bacteria or liquids; consumer products such as wind breakers, rainwear, sleeping bag liners, etc. However, the well known propensity of polyolefin articles to accumulate static charges is a disadvantage. Unfortunately, the conventional technique of simply applying antistat finishes to the nonwoven sheets does not ordinarily lead to a satisfactory solution, since even though certain of such finishes will adequately suppress static charge generation, they simultaneously confer a hydrophilic, rewettable character to the polyolefin nonwoven sheet,

and thus completely destroy its liquid water barrier property.

SUMMARY OF THE INVENTION

According to the present invention, we have discovered a limited class of agents having a balance of high antistat activity and moderate aqueous surfactant power such that they may be applied as a finish onto nonwoven sheets composed of polyolefin film-fibril elements to confer antistat protection without destruction of the sheets' inherent liquid water barrier (hydrophobic) properties.

The present invention concerns a nonwoven sheet comprised of film-fibril elements of an olefin polymer which sheet bears at least 0.1 percent by weight, preferably at least 0.3 percent by weight of a non-rewettable finish agent defined by the formula: $M_nR_{3-n}PO_4$ where M is selected from the group consisting of lithium, sodium, potassium, and ammonium ions, R represents an alkyl group containing 3 to 5 carbon atoms, and n is selected from the integers 1 and 2. The preferred agents are those where M represents the potassium ion, and the most highly preferred finish is a mixture of approximately equimolar quantities of the two agents potassium dibutyl phosphate and dipotassium butyl phosphate. The preferred polyolefin is linear polyethylene. It is preferred that at least 0.3 percent but no more than about 2 percent by weight of agent be present on the sheet. Excessive amounts of agent are not only unwarranted for economic reasons but are also undesirable because the water barrier properties of the sheet are adversely affected.

The antistat finish of this invention may be applied to the polyolefin nonwoven sheets by immersing the sheet in an aqueous solution of the agent; by kiss-roll, gravure roll, or similar application of a coating of an aqueous solution of the agent; or by spraying an aqueous solution of the agent onto the surface of the sheet. For those agents whose water solutions have surface tensions appreciably in excess of the critical surface tension of the polyolefin substrate, it is advantageous to lower the surface tension of the applied solution by addition of a third component such as a non-rewettable surfactant or a volatile alcohol.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The nonwoven fibrous sheets useful for this invention may be prepared from any crystalline olefin polymer but linear (high density) polyethylene is the preferred polyolefin. They are composed of film-fibril elements having a surface area greater than 2 meter²/gm. and may be produced by a flash extrusion method as disclosed in U.S. Pat. No. 3,169,899. The nonwoven sheets may be cold consolidated as described in said U.S. Pat. No. 3,169,899, or point embossed as disclosed in U.S. Pat. No. 3,478,141, or surface bonded type as disclosed in U.S. Pat. No. 3,442,740.

The operable agents for the finish/coatings of the present invention possess a critical balance of high antistat activity and moderate aqueous surfactant power. The mono and dialkyl phosphates wherein the alkyl group contains 3 to 5 carbon atoms (i.e., n-propyl, isopropyl, n-butyl, isobutyl, secondary butyl, tertiary butyl, n-amyl, and the various C₅ alkyl isomers) have been found to possess the required level of aqueous surfactant power to be useful in the present invention.

Although we do not wish to be bound by any theory, a working hypothesis consistent with the present invention is that the antistat agent must exhibit a certain level of aqueous surfactant power. If the antistat is too good a surfactant, then when the coated nonwoven sheet subsequently comes adventitiously in contact with water, a quantity of antistat will dissolve into the water to form a solution whose surface tension would be lower than the critical surface tension of the polyolefin substrate, and this solution will therefore wet the nonwoven sheet, penetrate the microscopic capillary channels between the individual film-fibril elements, and thereby destroy the liquid water barrier property of the sheet. This critical surfactant activity limit appears to be exceeded when the alkyl group of the alkyl phosphate antistat contains six or more carbon atoms. On the other hand, some minimum level of surfactant power is required of the antistat simply in order that it may be applied onto the nonwoven sheet (either by immersion, surface coating, spraying, etc.) from aqueous solution. The requirement is believed to be that the surface tension of the antistat solution should be such that the solution "almost wets" the nonwoven sheet. For example, in application of the antistat finish to linear polyethylene, the antistat solution should have a surface tension of about 37 ± 3 dynes/cm. A 0.2 - 1 percent aqueous solution of potassium amyl phosphate or a 1-2 percent solution of potassium butyl phosphate will satisfy this requirement directly. Potassium propyl phosphate, however, is not powerful enough a surfactant to meet this surface tension requirement at reasonable concentrations (less than 2 percent) in pure water, but it may successfully be applied to linear polyethylene from a 1 percent solution in a 17-volume percent isopropanol aqueous solvent (surface tension equal 35 dynes/cm.). In like fashion, sodium butyl phosphate and ammonium butyl phosphate are both somewhat poorer surfactants than potassium butyl phosphate so that their water solutions at less than 2 percent concentration fail to meet the surface tension requirement; but they too may successfully be applied to linear polyethylene from an alcohol/water solvent. Similarly, potassium butyl phosphate aqueous solutions at concentrations less than 1 percent have surface tensions which are too high (greater than 40 dynes/cm.), but such solutions can be made operable for coating linear polyethylene nonwoven sheets by adding a small quantity (e.g., 0.05 to 0.1 percent) of a non-rewettable surface active agent, such as "Igepal" CO-880 or CO-890 (registered trademark of GAF Corporation's nonionic nonylphenoxy polyoxyethylene ethanol surfactants). These materials are termed "non-rewettable" here in the sense that a linear polyethylene nonwoven sheet coated with these surfactants is not penetrated by a drop of water subsequently placed on the surface of the treated sheet.

The antistat finishes of the present invention may comprise a single agent of the formula: $M_nR_{3-n}PO_4$ (as previously defined) or it may be a mixture of such agents, e.g., potassium butyl phosphate plus potassium

isoamyl phosphate. Frequently mixtures are obtained directly in commercial operations. M may be chosen to be lithium, sodium, potassium, or ammonium ion but the potassium salts are preferred. The agent must contain at least one R group and at least one M group. It is to be noted that the finishes employed in this invention are not hydrophobic materials like the "water repellent" coatings conventionally applied to various woven and nonwoven fabrics in order to render them "waterproof," but are rather a very restricted group of antistat materials which may be applied to polyolefin film-fibril nonwoven sheets without destroying their inherent hydrophobic liquid water barrier property.

In the Examples which follow, all samples are prepared on a laboratory scale by immersing a portion of the nonwoven sheet material in an aqueous bath of the specified composition. The sheet is removed from the bath and passed through the nip of a pair of elastomeric squeeze rolls $2\frac{1}{8}$ inch (5.4 cm.) in diameter of 75 ± 5 Shore A Durometer hardness operated at a nip pressure of 4-8 pli to remove excess solution from the surface of the sheet. The wet sheet is then air dried followed by an additional two minutes drying period at 110°C . The antistat protection provided by the finish is determined by submitting the sample previously conditioned at least 24 hours at the indicated temperature and relative humidity to test NFPA (National Fire Protection Association) Code 56A, Section 25433, paragraph A, part 3. The result is reported as "Log R" with values of 11 (75°F . and 50 percent R.H.) being "passing" and lower values preferred. The water barrier performance of the sample is measured by two tests — the "hydrostatic head" test ASTM D-583, paragraph 53A, Method II, results reported in "inches" (cms.) with high values preferred; and the "rain penetration" test ASTM D-583, paragraph 32-37, results reported in "grams" with lower values preferred.

EXAMPLE I

This example illustrates the effect of varying the size of the alkyl groups of the phosphate antistat agents. Samples of nonwoven sheet comprising film-fibril elements of linear polyethylene are prepared by the process of U.S. Pat. No. 3,169,899 at a basis weight of approximately 2.2 oz./yd.² (75 gms./m.²) and subsequently bonded by the process of U.S. Pat. No. 3,442,740. These samples are treated with 0.5 weight percent aqueous solutions of various antistats as indicated in Table I. These antistats are all mixtures (approximately equimolar) of monopotassium dialkyl and dipotassium monoalkyl phosphate salts with the alkyl group indicated. At the 0.5 percent concentrations employed, potassium butyl phosphate, having the lowest surfactant power, can be successfully applied to the linear polyethylene substrate only by adding a small quantity of a surface tension depressant, in this case "Igepal" CO-890. This latter material by itself provides essentially no antistat protection for the linear polyethylene substrate.

TABLE I

Run	Antistat	Hydrostatic Head	Rain Penetration 2 ft./2 min. (61 cm/2 min)	Log R 75°F./55% RH
1-A	None	60 in. (152 cm.)	0 g.	>14
1-B	Potassium butyl phosphate*	50 in. (127 cm.)	0 g.	8.0
1-C	Potassium amyl phosphate	47 in. (119 cm.)	0.2 g.	8.1

TABLE I—Continued

Run	Antistat	Hydrostatic Head	Rain Penetration 2 ft./2 min. (61 cm/2 min)	Log R 75°F./55% RH
1-D	Potassium hexyl phosphate	31 in. (79 cm.)	3.6 g.	8.0
1-E	Potassium octyl phosphate	4 in. (10 cm.)	4.0 g.	7.5

*Plus 0.1% "Igepal" CO-890

Note that although all treated samples exhibit excellent antistat protection (values of Log R less than 11), the good liquid water barrier properties of the samples are lost when the size of the alkyl group is increased beyond the C₅ (amyl) limit of the present invention.

EXAMPLE II

This example illustrates the effect of changing the quantity of antistat agent applied as a finish to the nonwoven sheet. Samples of nonwoven sheet comprising film-fibril elements of linear polyethylene prepared by the process of U.S. Pat. No. 3,169,899 at a basis weight of approximately 1.3 oz./yd.² (44.2 gms./m.²) and subsequently embossed on one side with rows of point-bonds ("rib" pattern) and surface-embossed on the opposite side with a "linen pattern" (as in Examples VI and VII of U.S. Pat. No. 3,427,376) are treated with progressively higher concentration aqueous solutions of potassium butyl phosphate as indicated in Table II. At these high concentration levels of potassium butyl phosphate no third component surface tension depressant additive is required. Even though the heavier coat-

alkali metal or ammonium alkyl phosphate salts represent an approximately equimolar mixture of a salt containing one alkyl group with two alkali metal or ammonium ions and a salt containing two alkyl groups with one alkali metal or ammonium ion.

EXAMPLE III

This example illustrates the effect of various candidate antistat finishes, both within and outside the limitation of the present invention. All candidates are applied from a solution at the specified concentration, as indicated in Table III, in a solvent comprising 17 volume percent isopropanol in water such that in each case the surface tension of the solution is low enough to insure good wetting during application to the same linear polyethylene nonwoven substrate employed in Example II. Note that only the alkali metal and ammonium alkyl phosphates furnish good antistat protection (Runs 3A through 3I versus 3J and 3K), that presence of an alkyl group is essential (Run 3L), and that common quaternary alkyl ammonium halides are ineffective (Runs 3M through 3R),

TABLE III

Run	Antistat	Concentration	Log R 75°F (24°C)/55%RH Linen Side/Rib side
3-A	Potassium propyl phosphate	0.5 wt. %	13/11.9
3-B	do.	1.0	10/9.5
3-C	do.	2.0	9.0/8.5
3-D	do.	3.0	7.6/7.3
3-E	Potassium butyl phosphate	0.5	9.9-10.0/9.0-9.5
3-F	do.	1.0	8.9-9.0/8.4-8.7
3-G	do.	1.7	7.8/7.3
3-H	Sodium butyl phosphate	1.0	9.0/9.0
3-I	Ammonium butyl phosphate	1.0	9.0/9.0
3-J	Diethanolamine butyl phosphate	1.0	12-13/12-13
3-K	Guanidine butyl phosphate	1.0	13-14/13-14
3-L	Tri-potassium phosphate	3.0	>14/>14
3-M	Tetramethyl ammonium chloride	1.10	13/ 13
3-N	Tetramethyl ammonium bromide	1.54	13/ 13
3-O	Tetraethyl ammonium chloride	1.66	13/ 13
3-P	Tetraethyl ammonium bromide	2.10	13/ 13
3-Q	Tetrabutyl ammonium bromide	3.22	12/ 11
3-R	Tetrabutyl ammonium iodide	(sat. solution)	12/ 12

ings achieved with the more concentrated solutions do lead to small incremental improvements in antistat protection (lower values of Log R), the excellent water barrier property of the sheets is not destroyed.

TABLE II

Run	Conc. of Potassium Butyl Phosphate	Hydrostatic Head	Rain Pene. 2 ft/2 min.	Log R 70°F (21°C.)/ 55% RH
2-A	1.0 wt. %	41 in. (104 cm.)	0 g.	8.8
2-B	1.5	41 in. (104 cm.)	0	8.1
2-C	2.0	39 in. (99 cm.)	0	7.7
2-D	3.0	41 in. (104 cm.)	0	7.0
2-E	4.0	40 in. (102 cm.)	0	6.8
2-F	None	40-50 in. (102-127 cm.)	0	>14.0

In this example and in Examples III and IV which follow, it should be understood that each of the indicated

EXAMPLE IV

Products of the present invention are prepared as indicated at Table IV, employing the same linear polyeth-

ylene nonwoven substrate employed in Example II. The quantity of antistat finish on the treated sheet may be

determined either by standard analytical techniques (e.g., phosphorous or potassium analysis, using either chemical or spectroscopic techniques) or simply by calculating the amount of antistat contained in the quantity of treating solution picked up by the nonwoven sheet prior to drying, since the volatility of the antistat salts is very low.

The antistats are dissolved in water to the indicated weight percent, the sheet samples immersed in the solution and subsequently run through squeeze rolls at the indicated pressures, at which point the percent solution pickup is immediately determined by measuring weight gain, and the sample is then dried. The pickup of antistat, based on the dried sheet, is computed from the solution pickup and antistat concentration.

while permitting passage of water vapor, comprised of film-fibril elements having a surface area greater than 2 meter²/gm., said sheet bearing from 0.1 percent to 2 percent by weight of a finish defined by the formula: $M_n R_{3-n} PO_4$ where M is selected from the group consisting of lithium, sodium, potassium, and ammonium ions, R represents an alkyl group containing 3 to 5 carbon atoms, and n is selected from the integers 1 and 2.

2. The sheet of claim 1 bearing from 0.3 percent to 2 percent by weight of said finish.

3. The product of claim 1 wherein the finish is a mixture of approximately equimolar quantities of potassium dibutyl phosphate and dipotassium butyl phosphate.

TABLE IV

Run	Antistat	Conc.	Squeeze Roll Pressure	Solution Pickup	Antistat on Sheet	Log R
4A	Potassium Propyl Phosphate	2.5%	4.3 pli	20.5%	0.51%	8.8
4B	do.	5.0	do.	26.2	1.31	8.0
4C	Potassium Butyl Phosphate	1.5	8.5	26.	0.39	7.9
4D	do.	do.	do.	21.	0.32	7.9
4E	do.	2.0	do.	30.5	0.61	7.7
4E	do.	do.	do.	27.6	0.55	7.8
4G	do.	do.	do.	25.3	0.51	7.8
4H	do.	3.0	do.	30.5	0.91	7.35
4I	do.	do.	4.3	31.5	0.94	7.3
4J	do.	do.	do.	34.3	1.03	6.7
4K	Potassium Butyl Phosphate	0.5	do.	31.	0.16	7.8
	Igepal CO-890	0.1				
4L	do.	do.	8.5	25.	0.12	7.8

What is claimed is:

1. An antistatically protected nonwoven polyolefin sheet having inherent liquid water barrier properties

4. The product of claim 3 wherein the polyolefin is linear polyethylene.

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