

[72] Inventor **Joseph Edward Reardon**
Wilmington, Del.
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[73] Assignee **E. I. du Pont de Nemours and Company**
Wilmington, Del.
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Primary Examiner—Harold Ansher
Attorney—Robert W. Black

[54] **NON-WOVEN FIBROUS WEBS BONDED WITH**
CROSS-LINKED ETHYLENE/CARBOXYLIC ACID
COPOLYMERS AND METHODS OF MAKING
SAME
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ABSTRACT: Nonwoven fibrous webs bonded with a cross-linked and partially neutralized ethylene/alpha, beta-ethylenically unsaturated carboxylic acid copolymer are provided which possess high tensile strength and stiffness without substantial loss of these properties after repeated washing or drycleaning. The copolymer comprises about 55 to 97 percent by weight ethylene and about 3 to 45 percent by weight of the alpha, beta-ethylenically unsaturated carboxylic acid (methacrylic acid), about 0 to 75 percent of the acid groups neutralized. Cross-linking of the copolymer occurs with about 1 to 25 percent by weight, based on the weight of copolymer, of an epoxy resin or an amino-formaldehyde resin preferably cured at 180° C. for 1 minute. The copolymer imparts the improved properties to the nonwoven web whereas the cross-linking resin gives durability.

NON-WOVEN FIBROUS WEBS BONDED WITH CROSS-LINKED ETHYLENE/CARBOXYLIC ACID COPOLYMERS AND METHODS OF MAKING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 852,092, filed Aug. 21, 1969, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to nonwoven fibrous webs bonded with a polymeric binder, and more particularly to nonwoven fibrous webs bonded with cross-linked ethylene/alpha, beta-ethylenically unsaturated carboxylic acid copolymers.

2. Prior Art

Adequately bonded nonwoven webs have advantages over woven webs for a large variety of uses. Bonded nonwoven webs have heretofore been formed by impregnating, printing or otherwise depositing an adhesive bonding material on a web predominantly comprising relatively long fibers, including those of textile length of from about one-half inch to about $2\frac{1}{2}$ inches, or more. The web of nonwoven fibers, to which the binder is applied, can be produced inexpensively and with low capital investment by cording, garnetting, air-laying, paper-making procedures optionally followed by needle-punching procedures, or other known operations for which efficient automation is possible. The operation of bonding the fibers in place is much less expensive than conventional spinning and weaving.

The most commonly used binders for nonwoven webs directed to these uses have been either polyvinyl acetate, butadiene/acrylonitrile, acrylic or styrene/butadiene emulsions. Each of these binder systems has distinct shortcomings concerning either their stiffness, tensile or binding properties after being washed and/or drycleaned. As a result, the completely successful use of nonwoven webs for these uses has not been realized.

SUMMARY OF THE INVENTION

According to the present invention, there is provided an article comprising: a nonwoven fibrous web and a binder for said web comprising a copolymer of about 55 to 97 percent by weight ethylene and about 3 to 45 percent by weight of an alpha, beta-ethylenically unsaturated carboxylic acid, about 0 to 75 percent of acid groups neutralized with alkali metal ions, said copolymer cross-linked with about 1 to 25 percent by weight, based on the weight of copolymer, of an epoxy resin or an amino-formaldehyde resin. Nonwoven webs using the cross-linked copolymer as defined herein have very high tensile values both wet and dry before and after numerous cycles in conventional washing machines and also after drycleaning.

DESCRIPTION OF THE INVENTION

Any of the many techniques available for preparing nonwoven webs can be used in the present invention. In general, such techniques involve laying down a mass of fibers (usually 0.5 to 3 inches long) by methods, such as cording, garnetting and air laying, and then entangling the fibers to a certain extent. While for the present invention fiber entangling can be accomplished by any method, needle punching is particularly suitable. As described in a variety of articles (e.g., the July 1966 Modern Textiles Magazine, articles beginning on pages 20, 23, 28, 35 and 53, and the Dec. 1966 Textile Research Journal, article on page 1037), needle punching is comparatively simple and an especially advantageous method of preparing nonwoven webs with any of a variety of thicknesses, porosities and densities.

The nonwoven webs are prepared from natural or synthetic fibers, and preferably are composed of polyamide, polyester and acrylonitrile or blends thereof and with other natural and synthetic fibers.

The polymeric binder applied to the nonwoven web to bind the fibers is applied as an aqueous dispersion. Such aqueous dispersions are described in copending application Ser. No. 745,956, filed July 19, 1968, in the names of Joseph Edward Reardon and Vernon Clare Wolff, Jr., now abandoned, and assigned to the assignee of the present application, the contents of which are incorporated by reference.

Generally, the dispersion contains 20 to 60 percent solids of an ethylene/alpha, beta-ethylenically unsaturated carboxylic acid copolymer, and epoxy resin or an amino-formaldehyde resin as cross-linking agent and a cross-linking catalyst. The copolymer comprises about 55 to 97 percent by weight ethylene, preferably 70 to 95 percent; about 3 to 45 percent by weight of alpha, beta-ethylenically unsaturated carboxylic acid, preferably 5 to 30 percent of acrylic acid or methacrylic acid, with about 0 to 75 percent of the acid groups neutralized with alkali metal ions, preferably 10 to 50 percent neutralized with sodium from sodium hydroxide.

The cross-linking agents are the amino-formaldehyde and epoxy resins generally known in the art and available commercially and are employed in the dispersion at levels between about 1 and 25 percent by weight, based on the weight of copolymer, and preferably at levels between 2.5 and 10 percent. Melamine-formaldehyde resin is the preferred cross-linking agent, and the best results are obtained with it present at a level of about 7.5 percent. Best results are obtained with epoxy resins at about 5.5 percent.

The cross-linking catalyst is also present in the dispersion, and it is present at a level of about 1 to 25 percent by weight, based on the total weight of copolymer and cross-linking resin. The catalyst used will depend on the cross-linking resin used, but, generally, an ammonium salt of an acid, such as an ammonium halide, is the preferred catalyst for the amino-formaldehyde cross-linking resin. Its preferred concentration is about 5 to 15 percent. For the epoxy cross-linking resin, a polybasic organic amine is present in the dispersion at approximately the same concentration as given above.

As stated previously, the binder dispersion is applied to the web so as to impregnate or saturate it. Subsequently, the impregnated web is dried by passing the web through an air oven to evaporate the water and to cross-link the copolymer with the cross-linking resin. The catalyzed reaction cross-linking the epoxy resin and the partially neutralized ethylene copolymer, once initiated by heat upon drying, will continue to react at room temperature due to the catalytic effect of the partially neutralized ethylene copolymer molecule. Generally, any temperature-time relationship can be employed which is sufficient to remove the water and cross-link the copolymer. Usually, heating temperatures are within the range of 120 to 20° C. for a time within the range of 0.25 to 5 minutes. Normally, 180° C. for 1 minute is sufficient for curing. Those skilled in the art will recognize that economic considerations make the use of excessively long times undesirable, and the upper temperature limit is governed by the decomposition or shrinkage temperature of the fibers and/or binder. The dried and cured impregnated web will contain about 2 to 50 percent by weight of the cross-linked copolymer, preferably about 15 to 35 percent, based on the total weight of impregnated web.

Beside the above-stated advantage of retention of wet and dry tensile strength and stiffness, both before and after repeated washing and drycleaning, is the advantage of easily modifying the dispersion in order to vary the properties of the nonwoven fabric. For example, the tensile strength and stiffness of the partially neutralized copolymer impregnated web increases linearly with increasing neutralization of the acid groups to a value of about 45 percent neutralization and then remains essentially constant. The absolute value of these plateaus is dependent upon the weight percent of acid in the copolymer, since the stiffness and tensile properties are directly proportional to the amount of acid in the copolymer. This provides the manufacture of the nonwoven fabric the option of tailoring the properties of his product for the needs of the end user.

The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A 6 inch $\times$ 4 $\frac{1}{4}$ inch sample weighing 2 grams of a polyester nonwoven fabric was saturated with 250 grams of a 42 percent solids dispersion of a copolymer of 89 percent ethylene and 11 percent methacrylic acid (30 percent of acid group neutralized with sodium hydroxide). This dispersion also contained 10 grams of "Aerotex" M-3 (80 percent solids aqueous solution of melamine-formaldehyde condensate sold by American Cyanamid Co.), 7.5 ml. of concentrated ammonia and 75 grams of a 10 percent aqueous solution of ammonium bromide whose pH had been adjusted to 10 with concentrated

ing, and a dry tensile of 44 lbs./in. and a wet tensile of 34 lbs./in. after 10 wash cycles. The weight loss after the 10 washes was 3.03 percent.

EXAMPLES 2 TO 13

Using the procedures set forth in example 1, additional samples of polyester nonwoven fabric were prepared and tested. All of the dispersions contained about 7.5 percent of cross-linking resin and about 7.5 percent catalyst based on the weight of copolymer. The "Cymel" 301 cross-linking resin used in examples 4-6 and 10-12 is hexamethoxymethyl melamine sold by the American Cyanamid Co. The results are shown in table I. A bleached kraft paper towel and a spunbonded polyester fabric were saturated with the dispersion of example 4. Both of these materials had excellent durability and retained their stiffness after repeated washings.

TABLE I.—PROPERTIES OF POLYESTER NON-WOVEN WEBS BONDED WITH AMINE FORMALDEHYDE RESIN BEFORE AND AFTER WASHING

Example No.	Dispersion composition							Tensile, lbs./in.				After 10 washes, percent wt. loss
	Percent copolymer	Copolymer			X-link resin	Catalyst	Percent pickup	Before washing		After washing		
		Percent E	Percent MAA	Percent neutr.				Dry	Wet	Dry	Wet	
2	31.5	89	11	30	"Aerotex" M-3	NH ₄ Cl	21.61	31.00	31.25	20.00	15.00	4.32
3	31.5	89	11	30	do.	NH ₄ oxalate	11.28	33.00	33.00	30.00	12.00	2.36
5	31.5	89	11	30	"Cymel" 301	NH ₄ Br	32.25	50.00		31.50		0.00
6	31.5	89	11	30	do.	NH ₄ Cl	23.68	35.00		28.00		0.00
7	31.5	89	11	30	do.	NH ₄ oxalate	8.88	15.00		4.00		7.91
8	31.5	85	15	45	"Aerotex" M-3	NH ₄ Br	26.70	40.00		39.00		3.41
9	31.5	85	15	45	do.	NH ₄ Cl	42.82	51.25		38.00		0.00
10	31.5	85	15	45	do.	NH ₄ oxalate	37.95	45.50		37.50		2.03
11	31.5	85	15	45	"Cymel" 301	NH ₄ Br	37.54	40.00		22.00		0.31
12	31.5	85	15	45	do.	NH ₄ Cl	25.14	38.00		16.25		4.28
13	31.5	85	15	45	do.	NH ₄ oxalate	40.11	47.00		36.00		1.27
13	31.5	89	11	0	do.	NH ₄ Br	11.00	25.00		14.00		1.16

ammonia. The dispersion contains 7.5 percent of cross-linking resin and 7.5 percent based on the weight of copolymer. The fabric was patted between two paper towels and then between two fresh paper towels and placed through a wringer with 20 lbs. of weight applied. Curing of the saturated fabric was accomplished in a forced air oven at 180° C. for 1 minute. The add-on weight was determined and the percent pickup is the add-on weight, divided by the final weight of the cured fabric $\times$ 100. The tensile properties of the fabric were determined using an Instron Tensile Tester operated at a crosshead speed of 2 inches per minute on samples 6 inches long and 1 $\frac{1}{2}$ inches wide with a one-fourth inch notch midlength and perpendicular to the fabric. Wet tensile values were obtained after soaking the fabric for 1 minute in a 10 percent detergent solution (Mr. Clean) and then testing by the above method. The dura-

EXAMPLE 14

Using the dispersions of example 1 and example 13 to impregnate the nonwoven web described in example 1, different drying conditions were used to illustrate that drying must be at a temperature high enough or for a time long enough to give sufficient curing of the resin binder. The results are shown in table II. Samples A-G use the dispersion of example 1 and Samples H-L use the dispersion of example 13.

It is noted that samples A and D had inadequate cures due to insufficient times at temperature. Longer times at 120° C. will give an adequate cure; however, for commercial economics, a cure of 180° C. for 1 minute appears to be optimum since longer times at 180° C. do not appreciably increase tensile properties.

TABLE II.—THE EFFECT OF DRYING CONDITIONS ON TENSILE PROPERTIES BEFORE AND AFTER WASHING

Sample No.	Drying conditions			Tensile, lb./in.			
	Temp., ° C.	Time, min.	Percent pickup	Before washing		After washing	
				Dry	Wet	Dry	Wet
A	120	1	24.33	11.50	11.25	-----	-----
B	150	1	32.45	35.00	28.00	22.00	13.00
C (Ex. 1)	180	1	36.39	38.50	40.50	44.00	34.00
D	180	0.5	24.50	14.00	10.50	-----	-----
E	180	2	30.36	38.50	35.00	32.00	31.50
F	180	3	33.45	38.00	41.00	34.50	34.00
G	180	5	32.52	39.00	44.75	41.00	40.00
H	120	1	12.20	27.25	-----	19.00	-----
I	150	1	11.30	24.75	-----	8.00	-----
J	180	0.5	9.50	23.25	-----	5.00	-----
K (Ex. 13)	180	1	11.00	25.00	-----	14.00	-----
L	180	1.5	12.10	28.50	-----	25.50	-----

bility of the samples was tested after washing them 10 times in a conventional home washing machine using 20 grams of Tide detergent per washing cycle. The water temperature was set on hot for washing and on the warm setting for rinse. The cured fabric was found to be too stiff to be measured by a Drape Stiffness Tester.

The sample had a resin pickup of 36.39 percent a dry tensile of 38.5 lbs./in. and a wet tensile of 40.5 lbs./in. before wash-

EXAMPLES 15 TO 23

Example 1 was repeated except an epoxy resin (Genepoxy M-195, a bisphenol A epichlorohydrin based resin sold by General Mills) and its curing catalysts were substituted for the melamine-formaldehyde resin and its curing catalyst. As in example 1, the percent of epoxy resin and percent of catalyst are based on the weight of copolymer. The results are shown in table III.

TABLE III.—PROPERTIES OF POLYESTER NON-WOVEN WEBS BONDED WITH AN EPOXY RESIN BEFORE AND AFTER WASHING

Ex. No.	Dispersion composition						Percent pickup	Dry tensile, lbs./in.		Dry tensile, lbs./in. aged 1 week		After 10 washes percent wt. loss
	Percent copolymer	Copolymer			X-link resin, percent	Catalyst		Before, washing	After, washing	Before, washing	After, washing	
		Percent E	Percent MAA	Percent neutr.								
15.....	39	89	11	30	3.5	3.4% TETA ¹	26.50	20.00	30.00	42.50	26.00	1.37
16.....	39	89	11	30	5	3.5% TETA ¹	31.78	39.75	40.00	39.25	24.00	1.44
17.....	39	89	11	30	10	7% TETA ¹	24.67	47.00	46.25	35.00	25.50	0.78
18.....	39	89	11	30	3.5	3.4% V-25 ²	20.64	45.00	40.25	47.50	44.25	2.02
19.....	39	89	11	30	5	3.5% V-25 ²	22.76	37.50	31.25	35.00	29.00	0.02
20.....	39	89	11	30	10	7% V-25 ²	29.50	20.50	-----	35.00	34.00	5.6
21.....	29	85	15	60	20	None	42.87	41.50	34.50	47.75	26.25	8.00
22.....	39	89	11	20	3.5	3.0% V-15 ²	30.46	38.00	40.75	49.25	50.00	1.31
23.....	39	89	11	20	10	7% V-15 ²	25.31	38.00	31.00	32.00	42.50	6.16

¹ TETA, Triethylene tetramine.² V-15 and V-25, Shell Chemical Co. curing agents.

What is claimed is:

1. An article comprising: a nonwoven fibrous web and a binder for said web comprising a copolymer of about 55 to 97 percent by weight ethylene and about 3 to 45 percent by weight of an alpha, beta-ethylenically unsaturated carboxylic acid, up to about 75 percent of the acid groups neutralized with alkali metal ions, said copolymer cross-linked with about 1 to 25 percent by weight, based on the weight of copolymer, of an epoxy resin or an amino-formaldehyde resin.

2. The article of claim 1 wherein the nonwoven web comprises 98 to 50 percent by weight of said article and 2 to 50 percent by weight of binder.

3. The article of claim 2 wherein the copolymer comprises about 70 to 95 percent by weight ethylene and about 30 to 5 percent by weight acrylic acid or methacrylic acid, about 10 to 50 percent of the acid groups neutralized with alkali metal ions.

4. The article of claim 3 wherein the copolymer is cross-linked with a melamine-formaldehyde resin.

5. The article of claim 4 wherein the nonwoven fibrous web is comprised of fibers, and the article comprises about 15 to 35 percent by weight of binder.

6. In the process of preparing a polymer impregnated nonwoven fibrous web comprising applying to the web an aqueous dispersion of a polymer binder and thereafter heating the web to remove the water, the improvement comprising: (A) applying to the web an aqueous dispersion the solids of which com-

prise (1) a copolymer of about 55 to 97 percent by weight ethylene and about 3 to 45 percent by weight of an alpha, beta-ethylenically unsaturated carboxylic acid, up to about 75 percent of the acid groups neutralized with alkali metal ions, (2) about 1 to 25 percent by weight, based on the weight of the copolymer, of a cross-linking agent selected from the group consisting of an epoxy resin and an amino-formaldehyde resin, and (3) about 1 to 25 percent by weight based on total polymer solids, of a cross-linking catalyst comprising a polybasic organic amine when the cross-linking agent is an epoxy resin and an ammonium salt of an acid when the cross-linking agent is an amino-formaldehyde resin; and (B) heating the web at a temperature and for at time sufficient to remove the water and cross-link the copolymer.

7. The process of claim 6 wherein the dispersion saturated web is heated at a temperature within the range of 120 to 200° C., and for a time within the range of 0.25 to 5 minutes.

8. The process of claim 6 wherein the copolymer comprises about 70 to 95 percent by weight ethylene and about 30 to 5 percent by weight acrylic acid or methacrylic acid, about 10 to 50 percent of the acid groups neutralized with alkali metal ions.

9. The process of claim 8 wherein the cross-linking agent is a melamine-formaldehyde resin.

10. The process of claim 9 wherein the nonwoven fibrous web is comprised of fibers, and is impregnated with 2 to 50 percent by weight of polymer, based on the total weight of the impregnated web.