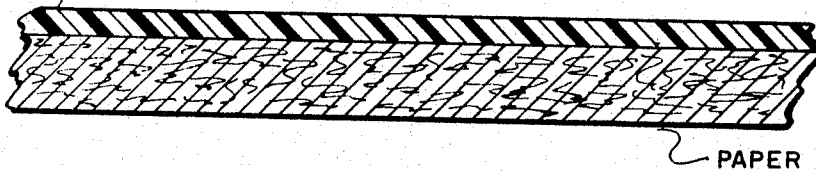


April 25, 1967

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PAPER CARRYING NON-BLOCKING FLEXIBLE
GREASE-PROOF VINYL POLYMER COATING
Filed Jan. 28, 1964

3,316,123

MIXTURE OF ETHYL ACRYLATE-ACRYLONITRILE COPOLYMER
AND THERMOSET AMINE-ALDEHYDE CONDENSATE



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3,316,123

PAPER CARRYING NON-BLOCKING FLEXIBLE GREASE-PROOF VINYL POLYMER COATING**Anthony Ralph Savina, Stamford, and Daniel Dickerson Ritson, Riverside, Conn., assignors to American Cyanamid Company, Stamford, Conn., a corporation of Maine**

Filed Jan. 28, 1964, Ser. No. 341,492

5 Claims. (Cl. 117—155)

This is a continuation-in-part of our copending applications Ser. Nos. 794,525 and 282,194, respectively filed on Feb. 20, 1959, and on May 15, 1963, and now abandoned.

The present invention relates to paper carrying on either or both sides a non-adherent grease- and water-resistant coating which is non-blocking at elevated temperatures. More particularly the invention relates to such paper coated with a homogeneous blend of an ethyl acrylate-acrylonitrile copolymer having a molecular weight in excess of about 1,000,000 and a thermoset amine-formaldehyde resin, as more particularly described below.

It is known that paper coated with a flexible copolymer of ethyl acrylate and acrylonitrile in weight ratio between about 4:1 and 6:5 is highly resistant to penetration by both grease and water making such paper particularly suited for fabrication into all-purpose containers, i.e., containers adapted to receive greasy and non-greasy liquids and solids at temperatures between about 0° C. and 100° C.

Paper of the type mentioned is often wound into rolls before use, and it is not uncommon for the rolls to be stored or shipped under conditions where the paper reaches an elevated temperature. Moreover, it is not uncommon for cups, plates, etc., fabricated from such paper (or manufactured by coating preformed paper containers with an appropriate coating composition of the copolymer) to be subjected to elevated temperatures for similar reasons.

A disadvantage of such paper is that before and after fabrication into useful articles it tends to "block" when maintained at elevated temperature, the layers or sheets adhering together because of the cohesiveness of the polymer. Paper which has blocked when stored in rolls tends to tear when unwound, and paper cups and plates which block tend to cause jamming when used in automatic apparatus dispensing hot food and drink.

The discovery has now been made that paper coated with a flexible grease- and water-resistant ethyl acrylate-acrylonitrile copolymer having a molecular weight in excess of about 1,000,000 possesses substantially no tendency towards blocking, even when maintained at temperatures as high as 190° F. for protracted periods of time, when the coating has a uniform substantial content of a thermoset amine-formaldehyde condensate.

The paper of the present invention is conveniently made by forming an aqueous emulsion of the ethyl acrylate-acrylonitrile copolymer, preferably by use of a sodium salt of a C₁₂-C₂₀ mono (higher fatty alcohol) sulfate as emulsifying agent, adding one or more thermosetting amine-aldehyde resins thereto, applying the product to one or both sides of the paper, and drying the paper at a temperature where the deposited emulsion copolymer particles coalesce and the condensate thermosets.

The structure of the coating on the paper has not been ascertained, but according to one theory it consists essentially of the thermoset amino resin set in a matrix of the copolymer, or the copolymer set in a matrix of the thermoset amino resin. The theory is presented for whatever help it may impart towards understanding the invention,

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and the invention does not depend on whether or not the theory is correct.

The paper-coating ethyl acrylate-acrylonitrile copolymer referred to is the known flexible, grease- and water-resistant polymer prepared by copolymerizing ethyl acrylate and acrylonitrile in weight ratio between about 4:1 and 6:5, and may contain minor amounts (less than about 5% of the weight of the two principal components) of vinyl monomers copolymerizable therewith, for example acrylic acid, acrylamide, vinylidene chloride, styrene, etc., to improve the properties of the copolymer as regards emulsification and to stabilize the emulsions thereby.

The amine-aldehyde condensate in the coating is a thermoset condensation product of an amidogen, for example melamine, urea, formoguanamine, thiourea, etc., with formaldehyde. Such condensates may be prepared by reacting a suitable amidogen at an alkaline pH with about 1 mol of formaldehyde for every aldehyde-reactive amino group present and continuing the reaction, if desired, at an acid pH until the syrup has increased in viscosity while remaining hydrophilic.

In the paper-coating emulsion the copolymer, being water-insoluble, is present as the dispersed phase and the hydrophilic amine-formaldehyde condensate is present in the aqueous phase. The emulsion need not contain an acid catalyst as the resins thermoset sufficiently rapidly for papermaking purposes, and in fact the emulsion may have an alkaline pH.

The viscosity of the emulsion chiefly depends upon the proportion of water present and is adjusted so as to fall within the range required by the particular coating method employed. The emulsion may be applied as a spray, or by doctor blade, off-set roll, or knife-coater, and is applied in sufficient thickness so that the final (dry) film weighs 1.5 to 1 lb. per 1000 ft.² of paper.

The final step in the process is the heating of the paper until the deposited polymer particles have coalesced and the amine-formaldehyde condensate has thermoset. The optimum heating temperature and the duration of the heating depend primarily upon the thermosetting characteristics of the particular amine-aldehyde resin employed and in each specific instance are most conveniently found by trial. It is preferred to heat the sheets at a temperature between about 220° F. and 300° F. for two minutes to five minutes as in this range the anti-blocking characteristics of the composition are developed without harm to the fibers.

Laboratory trials have shown that the presence of as little as 10% of the amine-formaldehyde condensate, based on the weight of the copolymer, improves the blocking characteristics of the copolymer, so that evidently a still smaller amount will impart some benefit. At the other extreme we have found it unnecessary for most practical applications to employ more than 75% of the condensate on the same basis, and the suitable amount in any one instance is most easily found by trial within or without the range mentioned.

In practice we prefer sufficient of the amino-formaldehyde condensate to give the coating composition a blocking rating of zero when tested under a pressure of 1 lb./in.² for 16 hours at 170° F. as this amount generally ensures that nested articles fabricated from this paper will separate readily when used in automatic dispensing equipment at elevated temperatures.

The invention is more particularly illustrated by the drawing which is a schematic vertical section of paper coated with a mixture of ethyl acrylate-acrylonitrile copolymer and a thermoset amine-aldehyde condensate.

The invention is more particularly described in the examples which follow. These examples constitute embodi-

ments of the invention and are not to be construed as limitations thereon.

Example 1

The following illustrates the effectiveness of amine-formaldehyde condensate in decreasing the high-temperature adhesiveness of paper coated with ethyl acrylate-acrylonitrile copolymer.

A series of coated papers were prepared on 50 lb. basis weight (25" x 40"/500 ream) stock by applying to one side of each sheet the ethyl acrylate-acrylonitrile emulsions with and without a thermosetting amine-aldehyde resin, as shown in the table below. The emulsions were applied at a thickness equivalent to 1.5 lbs. of resin solids per 1,000 square feet of paper surface by means of a 0.0005" Bird applicator at 40% resin solids. The paper samples were air dried and then heated in a circulating air oven for 2 minutes at 300° F. to cause the copolymer particles to fuse and the amine-aldehyde resin, where present, to thermoset.

The resin coatings were tested for blocking by the following modification of TAPPI standard T-477-m-47.

Squares 1" x 1" were cut from the coated paper samples and stacked in a constant temperature oven and a 1 lb. steel weight 1" x 1" in area was placed on top. The oven was maintained at 170° F. for 16 hours, at the end of which time the stack was separated into its components and the tendency of each pair of squares to block was noted. A blocking rating of 3 designates strong adhesion so that the coating is extensively torn when the sheets are peeled apart. A blocking rating of 2 designates local or slight adhesion of the coating so that only slight picking or marring occurs when the sheets are peeled apart. A blocking rating of 1 designates no actual adhesion but an affinity such that the surfaces do not slide freely against each other, or an audible "tick" is heard when the sheets are peeled apart. A blocking rating of 0 designates separation of the surfaces without adhesion or tick, that is, as if the surfaces were enameled so that they fall apart.

The emulsions were prepared by emulsion copolymerizing ethyl acrylate and acrylonitrile in 70:30 weight ratio in water containing catalyst and emulsifying agent [Duponal C (sodium lauryl sulfate)]. One portion of the product was reserved as control and to this nothing was added. To the remaining portions were added sufficient of 40% by weight aqueous solutions of a melamine-formaldehyde condensation [di (methoxymethyl) hydroxymethylmelamine] and a urea-formaldehyde condensate (the urea-formaldehyde-bisulfite resin of U.S. Patent No. 2,559,578) to supply the proportions of these resins shown in the table below.

Results were as follows:

Run No.	Sheet Assembly	Amino CH ₂ O Resin		Block Test, 1 lb./in. ² , 16 hrs.	
		Type	Percent ¹	Temp., ° F.	Rating ²
A ³	Face to face	-----	None	170	2
B ³	Face to back	-----	None	170	2
1	Face to face	Mel	25	170	0+
2	Face to back	Mel	25	170	0
3	Face to face	Mel	50	170	0
4	Face to back	Mel	50	170	0
5	Face to face	Urea	25	170	0
6	Face to back	Urea	25	170	0
7	Face to face	Urea	50	170	0
8	Face to back	Urea	50	170	0
9	Face to face	Urea	65	190	0

¹ Based on the weight of ethyl acrylate-acrylonitrile copolymer.

² See text above.

³ Controls.

Similar results are obtained by use of other sodium salts of C₁₂-C₂₀ mono(higher fatty alcohol) sulfates. These sulfate ester-salts are present in the vinyl coating composition and act as secondary anti-blocking agents, enhancing the primary anti-blocking effect produced by the thermoset amine-formaldehyde condensate.

Example 2

Coated paper was prepared by repetition of the method of Example 1 except that the latex was applied from a 0.0003" Bird applicator, the coating being equivalent to about 1.25 lbs. of total resin solids per 1,000 sq. ft. of paper, the latex being applied as a double coating to give this thickness of resin.

The paper sheets were dried according to the method of Example 1 and were tested for grease resistance according to TAPPI Standards Test T-454-m-44, wherein small (approximately 5 gm.) cones of sand are formed on the paper and grease resistance is determined as the number of minutes required for 1.1 ml. of turpentine (containing an oil soluble red dye) added to each cone to penetrate the sheet. The endpoint of the test is the time for first penetration, and observations are discontinued after 480 minutes because of evaporation of turpentine. In this test, resistance of coating material at the very thin film thickness described above to penetration by turpentine for the full 480 minute period is regarded as excellent.

Results were as follows:

Run No.	Amino CH ₂ O Resin		Grease Resist. (minutes)
	Type	Percent ¹	
A ²	-----	None	>480
1	Mel	25	>480
2	Mel	50	>480
3	Urea	25	>480
4	Urea	50	>480

¹ Based on weight of ethyl acrylate-acrylonitrile copolymer.

² Control.

Example 3

The following illustrates the decreased blocking possessed by cups formed of paper according to the present invention after nesting at elevated temperature under weight.

A number of uncoated paper cups were half-filled with the emulsion of Example 1 wherein the amino-aldehyde resin was di(methoxymethyl) hydroxymethylmelamine, slowly spun so as to coat the interior surface of the cups with the emulsion, emptied, and then spun at 1700 r.p.m. to remove excess emulsion. The cups were then oven dried for 2 minutes at 300° F. and had uniformly coated interiors and lips.

The cups were nested and tested in groups of five, the top cup in each stack being weighted with sufficient sand so that the bottom cup sustained a weight equal to the weight of 49 cups. The stacks of cups were placed in an oven at 190° F. for 24 hours and blocking values were assigned by lifting the stacks, releasing the cups consecutively from the bottom, and averaging the results. The block ratings assigned correspond to those of Example 1.

Run No.	Percent Mel. CH ₂ O Resin ¹	Block Test (50 cup equiv., 190° F., 24 hrs.)
A ²	None	2
1	25	1
2	50	0

¹ Based on the weight of ethyl acrylate-acrylonitrile copolymer.

² Control.

Example 4

The procedure of Example 2 was repeated except that the amine-aldehyde condensate was the reaction product of hexakis (methoxymethyl) melamine with 33% by weight of glycerol. Results obtained were substantially the same.

Example 5

It is necessary that the molecular weight of the copoly-

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mer component of the coating be in excess of about 1,000,000 because laboratory work has shown that when the copolymer content of the coating has a materially lower molecular weight, the coating possesses significant blocking properties. Laboratory work has further shown that these blocking properties are not counteracted by even large amounts of the amine-aldehyde component.

The foregoing is illustrated as follows:

The procedure of Example 1 is repeated, except that copolymers are used having the molecular weights shown in the table below, and the amine-aldehyde resin is a melamine-formaldehyde resin.

Results are as follows:

Run No.	Copolymer Molec. Wt. ¹	Percent Amine CH ₂ O Resin ²	Sheet Assembly	Rating Block Test ³
1-----	700,000	50	Face to face-----	2+
2-----	700,000	65	-----do-----	2
3-----	1,300,000	50	-----do-----	0
4-----	1,300,000	25	-----do-----	0+

¹ Weight average molecular weight determined at 35°, 40°, 45°, 50°, 90° and 135° for each of six solution concentrations, by procedure of Stacey, "Light Scattering in Physical Chemistry," Academic Press, N. Y., 1956, and Brice-Phoenix Light Scattering Photometer Operation Manual OM-1000, Phoenix Precision Instrument Co., Philadelphia, Pa., 1955.

² Based on weight of copolymer.

³ By method of Example 1.

Comparison of run 1 with run 2 shows that coatings wherein the copolymer has a molecular weight substantially below 1,000,000 possess very significant blocking properties, and that these blocking properties are not significantly affected by a substantial increase in the amount of amine-aldehyde.

Comparison of these runs with run 3 show that the blocking problem substantially disappears when the copolymer in the coating has a molecular weight in excess of 1,000,000. Run 4 shows that it is the molecular weight which is of primary significance because the block test rating of the coating does not significantly change even when the amount of amine-aldehyde resin in the coating is greatly decreased.

What is claimed is:

1. Paper coated on at least one side with a flexible uniform grease- and water-resistant composition consisting essentially of ethyl acrylate and acrylonitrile copolymerized in weight ratio between 4:1 and 6:5 to a molecular weight in excess of 1,000,000, and a thermoset amine-formaldehyde condensate in amount between 10% and 75% of the weight of said ethyl acrylate and acrylonitrile copolymer as anti-blocking agent.

2. Paper coated on at least one side with a flexible uniform grease- and water-resistant composition consist-

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ing essentially of ethyl acrylate and acrylonitrile copolymerized in weight ratio between 3:1 and 3:2 to a molecular weight in excess of 1,000,000, and a thermoset amine-formaldehyde condensate in amount between 10% and 75% of the weight of said ethyl acrylate and acrylonitrile copolymer as anti-blocking agent.

3. Paper coated on at least one side with a flexible uniform grease- and water-resistant composition consisting essentially of ethyl acrylate and acrylonitrile copolymerized in weight ratio between 3:1 and 3:2 to a molecular weight in excess of 1,000,000, and a thermoset melamine-formaldehyde condensate in amount between 10% and 75% of the weight of said ethyl acrylate and acrylonitrile copolymer as anti-blocking agent.

4. Paper coated on at least one side with a flexible uniform grease- and water-resistant composition consisting essentially of ethyl acrylate and acrylonitrile copolymerized in weight ratio between 4:1 and 6:5, a thermoset amine-formaldehyde condensate in amount between 10% and 75% of the weight of said ethyl acrylate and acrylonitrile copolymer, and a sodium salt of a C₁₂-C₂₀ mono (higher fatty alcohol) sulfate as secondary anti-blocking agent.

5. Paper coated on at least one side with a flexible uniform grease- and water-resistant composition consisting essentially of ethyl acrylate and acrylonitrile copolymerized in weight ratio between 4:1 and 6:5, a thermoset amine-formaldehyde condensate in amount between 10% and 75% of the weight of said ethyl acrylate and acrylonitrile copolymer, and sodium lauryl sulfate as secondary anti-blocking agent.

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