## **United States Patent**

### Kasugai et al.

3,660,142 [15] May 2, 1972

[54]	METHOD OF MAKING A PHOTOGRAPHIC BASE MATERIAL	[:
[72]	Inventors: Tsuneo Kasugai, Shizuoka; Wataru Ueno, Kanagawa, both of Japan	3
[73]	Assignee: Fuji Photo Film Co., Ltd., Ashigara- Kamigun, Kanagawa, Japan	3
[22]	Filed: <b>June 9, 1970</b>	P A
[21]	Appl. No.: 44,872	A
[30]	Foæign Application Priority Data	[:
	June 9, 1969 Japan44/45271	Ir C
[52]	U.S. Cl117/93.1 CD, 117/155 UA, 117/161 UF, 204/168, 264/22, 260/501.13, 260/534 M	fo
[51]	Int. Cl	
[58]	Field of Search117/93.1 CD, 155 UA, 161 UF;	
	204/168; 264/22; 260/534 M, 501.13	

#### 56] References Cited

# **UNITED STATES PATENTS**

[45]

3,061,882 11/1962 Wolinski......204/168 X 3,448,128 6/1969 Marumo et al......260/501.13 X 1/1971 3,555,079 Marumo et al. .....260/501.13

Primary Examiner—Alfred L. Leavitt Assistant Examiner—J. H. Newsome

Attorney-Sughrue, Rothwell, Mion, Zinn and Macpeak

#### ABSTRACT

Improving the wettability of photographic base material by incorporating therein a small amount of a compound having the formula

9 Claims, No Drawings

## METHOD OF MAKING A PHOTOGRAPHIC BASE MATERIAL

#### **BACKGROUND OF THE INVENTION**

#### 1. Field of the Invention

This invention relates to a method of making a photographic base material.

2. Description of the Prior Art

The principal object of this invention is to improve the wettability of a photographic base material, such as polyethylene film or polyethylene laminated paper, by undercoating solutions and light-sensitive emulsions.

Since polyethylene possesses very low polarity and wettability by water, as is well known, the use of polyethylene film or polyethylene-coated paper as photographic base materials encounters the disadvantages that light-sensitive emulsions or undercoating solutions cannot be coated uniformly, since sufficient adhesion of the light-sensitive emulsion or undercoating layers to the polyethylene surface cannot be obtained.

For the purpose of overcoming these disadvantages, British Pat. No. 971,058 discloses that the contact angle of water to the polyethylene surface is reduced by electron radiation. The reduction of the contact angle which can be obtained by this method, however, is limited and it is very difficult to reduce the contact angle to less than 50°.

#### SUMMARY OF THE INVENTION

Applicants have found that reduction of the contact angle below this level can be obtained by incorporating in the 30 polyethylene a small amount of a material having the following structural formula,

in which R is a hydrocarbon group, preferably an alkyl group of eight to 22 carbon atoms, R' is hydrogen or a lower alkyl group, M is an organic amino group or a metal, p and q are integers, preferably from one to five, x is preferably from one to three, y is preferably one, or, when M is a metal, x and y are numbers determined by its valence, followed by the preparation of a base material having a surface comprising this mixture, such as a film or laminated paper, and subjecting such surface to a corona discharge treatment.

As organic amino groups represented by R in the above formula, there may be mentioned alkyl amino groups, such as diethylamino and butylamino, alkanolamino groups, such as diethanolamino and propanolamino and the like.

As metals represented by R in the above formula, there may be mentioned such metals as calcium, magnesium, aluminum, tin, zinc, iron, copper, lead, barium and the like.

Although the above mentioned material (I) has the effect of improving the wettability of polyethylene, the addition of larger amounts of such compounds to polyethylene tends to 60 result in a deterioration of the adhesiveness of the polyethylene to light-sensitive emulsion or undercoating layers. Therefore, the amount thereof to be added is limited.

In accordance with the method of the present invention, however, it is possible to improve effectively the wettability of the surface of a polyethylene film or polyethylene laminated paper by light-sensitive emulsions without lessening the adhesiveness thereto.

Material in accordance with the foregoing structural formula (I) can be synthesized by reacting a higher alkylamine with thylene oxide of propylene oxide, reacting the product with monochloroacetic acid or its sodium salt and subjecting the resulting reaction product to neutralization with an organic amine, or to double decomposition, to thus obtain the corresponding salt. The following reaction schema illustrates this process.

$$\begin{array}{c} (CH_{2}CH_{2}O)p\Pi \\ RNH_{2} + nCH_{2} - CH_{2} \longrightarrow RN \\ \\ (CH_{2}CH_{2}O)q\Pi \\ (CH_{2}CH_{2}O)pH \\ RN \\ + CICH_{2}COOH \longrightarrow RN^{+} \\ (CH_{2}CH_{2}O)qH \\ \\ (CH_{2}CH_{2}O)qH \\ \\ (CH_{2}CH_{2}O)pH \\ RN^{+} \\ + NH(CH_{2}CH_{2}OH)_{2} \longrightarrow \\ (CH_{2}CH_{2}O)pH \\ RN \\ CH_{2}COO^{-} \\ (CH_{2}CH_{2}O)qH \\ \\ (CH_{2}CH_{2}O)qH \\ \\ (CH_{2}CH_{2}O)qH \\ \\ (CH_{2}CH_{2}O)pH \\ \\ RN \\ OH \\ CH_{2}COONH_{2}(CH_{2}CH_{2}O)pH \\ \\ RN \\ CH_{2}COONH_{2}(CH_{2}CH_{2}O)pH \\ \\ RN \\ CH_{2}COONH_{2}(CH_{2}CH_{2}O)pH \\ \\ RN \\ CH_{2}COONA \\ \\ (CH_{2}CH_{2}O)qH \\ \\ CH_{2}COOO \\ \\ \end{array}$$

Examples of the synthesis of compounds in accordance with formula (I) are are as follows:

#### SYNTHESIS EXAMPLE 1

5 183 g of lauryl amine was placed in a glass flask equipped with a stirrer and heated to 130°C under atmospheric pressure. 220 g of ethylene oxide was then blown into the flask and the temperature decreased to 100°C. 118 g of sodium monochloroacetate was then added and the mixture maintained at 100°C for 3 hours. The reaction mixture was then neutralized with 106 g of diethanolamine and cooled, whereby the following product was obtained.

#### **SYNTHESIS EXAMPLE 2**

Following the procedures of Synthesis Example 1, lauryl amine was reacted with ethylene oxide and then with sodium monochloroacetate. The product was then double-decomposed with barium chloride.

#### SYNTHESIS EXAMPLE 3

Following the procedures of Synthesis Example 1, stearyl amine was reacted with ethylene oxide and then with sodium monochloroacetate. The product was then double-decomposed with barium chloride to obtain the following compound.

$$\begin{bmatrix} (\text{CII}_2\text{CH}_2\text{O})\text{pH} \\ \text{C}_{18}\text{H}_{37}-\text{N}-(\text{CII}_2\text{CII}_2\text{O})\text{qH} \\ \text{OII} & \text{CH}_2\text{COO} \end{bmatrix}_2 \text{Ba} \qquad (p+q=4)$$

#### **SYNTHESIS EXAMPLE 4**

Following the procedures of Synthesis Example 1, stearyl amine was reacted with ethylene oxide and then with sodium monochloroacetate. The product was then double-decomposed with calcium chloride to obtain the following compound.

#### **EXAMPLE 2**

0.15 Part by weight and 0.3 part by weight of material B, represented by the formula,

were mixed, respectively, with 100 parts of high density polyethylene resin pellets manufactured by Showa Denko Co., Ltd. (Sholex 6050, having a density [ASTM-D-1505-60T] 0.960 and a melt index [ASTM-D-1238-57T] of 5.0) and then formed into films of about 0.1 mm in thickness by the use of a T-die type extruder of 65 mm.  $\phi$ . Similarly, a material B-free film was prepared for comparison.

The contact angle was measured for the resulting samples, before and after being subjected to discharge treatment at 180 W by the same apparatus as that of Example 1, to obtain the results tabulated below.

Sample	No discharge treatment	Discharge treatment
No material B present	93°	72 °
0.15 part of material B	85°	47 °
(to 100 parts of polyethylene) 0.3 part of material B	76°	32°
(to 100 parts of polyethylene)		

After the foregoing samples were respectively coated with a photographic light-sensitive emulsion and dried, the adhesive strengths of the emulsions to the polyethylene surfaces were measured to obtain the results tabulated below (by a Schopper's tension tester).

,	Sample	No discharge treatment	Discharge treatment
	No material B	15 g/10 mm	53 g/10 mm
	0.15 part of material B		
	(to 100 parts of polyethylene)	14	66
	0.3 part of material B		
	(to 100 parts of polyethylene)	no adhesion	51

The photographic light-sensitive emulsion employed above was prepared from a mixture of 70 g of gelatin, 62 g of a silver halide (65 mol % AgC1, 35 mol % AgBr) having an average particle size of 0.1 micron and sufficient water to make 1000 cc. The method of preparing the emulsion was conventional and included sensitization with sulphur and a gold salt and the incorporation of saponin as a wetting agent and formaldehyde as a hardening agent, as is well known in the art. The pH of the prepared emulsion was 6.0.

What is claimed is:

40

65

1. A method of making a photographic base material, comprising subjecting to corona discharge treatment a base material, the surface of which comprises polyethylene containing a compound represented by the general formula,

70 in which R is a hydrocarbon group of eight to 22 carbon atoms, R' is hydrogen or a lower alkyl group, M is an organic amino group or a metal, p and q are integers, x and y are numbers and, where M is a metal, numbers determined by its valence.

 The method of making a photographic base material according to claim 1, wherein said base material is polyethylene.

(CII<sub>2</sub>CII<sub>2</sub>O)pH C<sub>18</sub>II<sub>37</sub>-N-(CH<sub>2</sub>CII<sub>2</sub>O)qH OH CH<sub>2</sub>COO

Any of these compounds may be blended in polyethylene in accordance with this invention. A very small amount of these compounds is sufficient to achieve the object of the invention. Preferred amounts to be incorporated are 0.3 to 0.5% by weight based on the weight of the polyethylene. In the case of a polyethylene laminated paper, it has been found that the addition of more than 1% by weight results in gradual deterioration in the adhesiveness between the polyethylene and the paper, although wetting by an emulsion or undercoating agent coated thereon is improved. The advantages of this invention can be realized, however, even at proportions exceeding 1%, 15 to some extent. Moreover, the lower limit may be extended, for example, to about 0.1%. Addition of the compound may, as occasion demands, be carried out after it is dispersed or dissolved in a high boiling organic solvent. The compound, after being added to the polyethylene, is kneaded therewith in an 20 extruder such as those used in film making or film applying.

The photographic base material of the present invention is a base material, the surface of which, at least, comprises polyethylene containing the foregoing compound. As examples of such materials may be mentioned polyethylene film and polyethylene-coated paper, cloth, wood and metal. In the method of the invention, this base material is subjected to a corona discharge, whereby the wettability of the polyethylene surface by light-sensitive emulsions and aqueous undercoating solutions is improved.

The following examples are presented in order to further illustrate the invention without limiting the same.

#### EXAMPLE 1

0.3 Part by weight of material A, represented by the formula

$$\begin{bmatrix} (CH_2CH_2O)_2H \\ C_{12}H_{23} - N - (CH_2CH_2O)_3H \\ HO & CH_2COO \end{bmatrix}_2$$

was mixed with 100 parts of polyethylene resin pellets manufactured by Nippon Unicar Co., Ltd. (NUC-8008, having a density [ASTM-D-1505-60T] of 0.918 and a melt index [ASTM-D-1238-57T] of 5.0) and extruded and applied at 30°C. to a raw base paper of 180 g/m², so as to provide a film thickness of about 30 microns, by the use of a T-die extruder. For comparison, a laminated paper was prepared using the polyethylene free from material A. The contact angle with water was measured for both the samples, before and after being subjected to corona discharge treatment.

The corona discharge treatment was carried out at a discharge power of 35 W, 70 W and 180 W by means of a discharge apparatus made by Lepel Highfrequency Laboratories, Inc. while moving polyethylene laminated paper of 30 cm in width at a rate of 10 m/min through an air gap of 0.8 mm.

The contact angles of water to the surface of the laminated papers treated as above are tabulated below.

Sample	No. discharge	35 W	70 W	150 W
Comparison sample- polyethylene alone	94°	71 °	67°	66°
A-containing polyethylene	60°	42°	16°	7°

The measurement of the contact angle was carried out after 60 seconds by the dropping of about 0.001 cc of distilled water and using a contact angle meter of the Goniometer type, model G-1, made by Erma Optical Works Ltd.

When a 2% aqueous solution of gelatin as an undercoating solution was coated onto the foregoing samples at a rate of 25 m/min, only the samples in which the contact angle had been reduced to 50° or less by the method of this invention exhibited good wettability.

10

3. The method of making a photographic base material according to claim 1, wherein said base material is a polyethylene coated paper.

4. The method of making a photographic base material according to claim 1, wherein said compound is one having the 5 following formula,

5. The method of making a photographic base material according to claim 1, wherein said compound is one having the following formula,

6. The method of making a photographic base material according to claim 1, wherein said compound is one having the following formula,

7. The method of making a photographic base material according to claim 1, wherein said compound is one having the following formula,

$$\begin{bmatrix} (\text{CH}_2\text{CH}_2\text{O})\text{pH} \\ \text{C}_{18}\text{H}_{37}-\text{N}-(\text{CH}_2\text{CH}_2\text{O})\text{qH} \\ \text{OH} & \text{CH}_2\text{COO} \end{bmatrix}_2^{\text{Ca}} \quad (p+q=4)$$

8. The method of making a photographic base material according to claim 1, wherein the amount of said compound to be added is 0.3 to 0.5% by weight, based on the amount of said polyethylene.

9. The method of making a photographic base material according to claim 1, wherein the amount of said compound to be added is 0.1 to 1.0% by weight, based on the amount of said polyethylene.

25

30

35

40

45

50

55

60

65

70