

July 30, 1957

G. F. NADEAU ET AL.
REMOVABLE LAYERS FOR FILM

2,801,191

Filed Nov. 8, 1955

Fig. 1

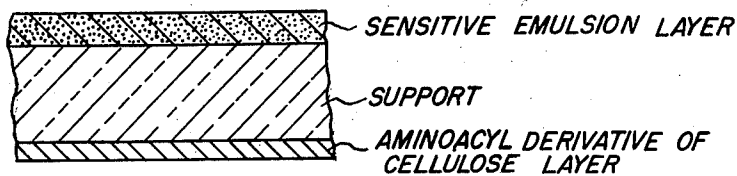
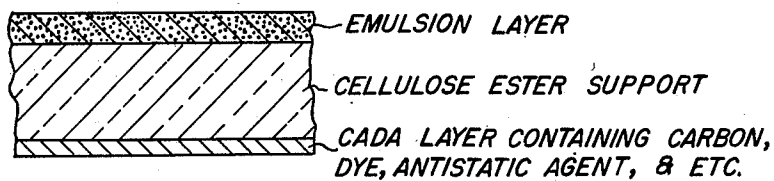


Fig. 2



GALE F. NADEAU
CRAYTON B. THOMPSON
INVENTORS

BY *Daniel J. Mayne*
Harold N. Powell

ATTORNEYS

1

2,801,191

REMOVABLE LAYERS FOR FILM

Gale F. Nadeau and Crayton B. Thompson, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Application November 8, 1955, Serial No. 545,644

10 Claims. (Cl. 117—138.8)

This invention relates to backed film or sheeting. More particularly this invention concerns photographic film carrying a new and improved backing.

As is well-known, film or sheeting quite frequently has backing or coating thereon. For example, photographic film is, in many instances, provided with a coating or layer on one or more of the surfaces, such as a layer or layers known as antihalation backings, antistatic layers and the like. These layers, which are provided for such purposes as aforementioned, in many instances for best performance should be relatively permanent for a period, such as during manufacturing operations, but should be capable of being removed.

For example, in the instance of photographic film it might be desired that the antistatic or antihalation backing remain on the film during manufacture and processing of the film. However, when a finished negative is produced it would be desired that such backings be eliminated.

Certain of the backings heretofore in use have presented problems either in difficulty of removal or in that special care has been required in the manufacture and handling of the film backed in accordance with practices prior to the present invention, so that the backing did not become removed prematurely.

It is apparent, therefore, that the development of a backing which not only satisfactorily performs the desired function such as performing as an antihalation backing, antistatic backing or the like, but which lends itself to removability at the proper time, represents a highly desirable result. We have found a material and its method of application to film and sheeting, as will be described in detail hereinafter, which constitutes an especially useful and improved backing on film and sheeting.

This invention has for one object to provide a film or sheet backed with a removable backing. Another object is to provide a photographic film carrying a new and improved removable backing. Still a further object is to provide a film or sheet carrying a backing which is relatively easily removable in a slightly acid media. Still another object is to provide a method of applying aminoacyl cellulose derivatives to photographic films as backings. Another objects is to provide a method for the aforesaid whereby the aminoacyl derivative may contain various additives such as dyes, pigments and/or conducting agents. A particular object is to provide a photographic film of cellulose acetate with an aminoacyl cellulose derivative backing. Other objects will appear hereinafter.

We have found that there are certain aminoacyl derivatives of cellulose which possess the unique quality of being soluble in slightly acid media. We have further found that these aminoacyl derivatives may be applied as coatings to films and sheets to provide various type layers and backings such as antihalation and antistatic backings, for example. These layers or coatings, because of the acid solubility as aforementioned, provide a backing that may be relatively readily removed as desired. That is, the backing may be removed by a slightly acid media such

2

as for example a 0.5% glacial acetic acid solution without damage to the film product.

For a more complete understanding of our invention reference is made to the attached drawing. In the drawing,

5

Fig. 1 is a diagrammatic, sectional view on an enlarged scale, generally illustrating a film product in accordance with the present invention.

10

Fig. 2 likewise is a diagrammatic, sectional view on an enlarged scale, illustrating a species of the film product of the present invention.

Specific examples of some of these aminoacyl cellulose derivatives which are useful in the present invention are as follows:

15

Cellulose acetate N,N-dimethylamino acetate

Cellulose acetate N, N-diethylamino acetate

Cellulose acetate N,N-dipropylamino acetate

Cellulose acetate morpholino acetate

20

Cellulose acetate butyrate N,N-diethylamino acetate

Ethyl cellulose N,N-diethylamino acetate

25

In order to obtain aminoacyl derivatives of the class indicated having the desired properties for backing purposes in accordance with the present invention, certain procedures are preferably used in the preparation of such compounds. That is, the intermediate cellulose acetate chloroacetate used in the manufacture of the aminoacyl compounds preferably will have at least a 4% chlorine (halogen) content. On amination of the final aminoacyl cellulose derivative will then have at least 1½% nitrogen.

30

The following description illustrates one method for the preparation of compounds such as may be employed in the present invention. It is to be understood, however, that while we prefer to use the CADA compounds prepared in accordance with the procedures which will be set forth, this is not to be regarded as a limitation on our invention. That is, CADA compounds, provided they have the desired composition and properties as above disclosed, even if prepared by other methods, would be within the scope of the present invention.

40

In making the compounds used in the present invention, halogen-containing cellulose derivatives would be one of the starting materials. For example, halogen-containing cellulose derivatives such as cellulose acetate chloroacetates and ethylcellulose chloroacetates are illustrative. Other cellulose derivatives containing other acyl and chloroacetyl, chloropropionyl and the like may also comprise starting materials. As to methods for preparing halogen-containing cellulose derivatives, reference may be made to the literature, i. e. Malm, Mench, Williams and Hiatt, Ind. Eng. Chem., 42, 1547 (1950).

50

The halogen-containing cellulose derivatives illustrated by cellulose chloroacetate in the dry condition and containing at least 4% of chlorine, is dissolved in a solvent such as dioxane, acetone, methyl ethyl ketone, or other suitable solvent. There is then added at least two molar equivalents of a secondary amine based on the chlorine content of the cellulose derivative. This amount supplies one mole of amine to replace the chlorine atom and another mole to form amine hydrochloride which is insoluble in the reaction solvent and effectively removes the HCl liberated. This facilitates the forcing of the amination reaction to completion and also prevents degradation of the cellulose ester by the liberated acid. Secondary amines which may be used for the formation of desirable dilute acid-soluble cellulose derivatives include dimethylamine, diethylamine, di-n-propylamine, di-isopropylamine, di-n-butylamine, morpholine, piperidine and the like. Mixed secondary aliphatic amines also may be utilized in some instances. However, it should be noted that while the higher aliphatic secondary amines and the aromatic amines or the mixed aromatic-aliphatic

60

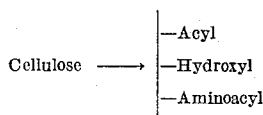
65

70

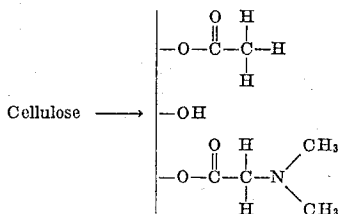
amines readily undergo the amination reaction, that cellulose derivatives may be obtained which are not as soluble in dilute aqueous acids as is desired. Accordingly, in preparing the products for the present invention care will be taken in this respect as to using amines which do result in the desired acid soluble product.

The reaction of the amine with a cellulose derivative may be accomplished by refluxing the components together in the above-identified solvent environment. The reaction may take several hours depending on the particular amine and the like factors. After completion of the reaction the aminated product may be isolated by dilution of the solvent and precipitation into water. The precipitation product may be washed or otherwise processed to bring it to the desired degree of purity and freedom from solvent, then dried and placed in a condition for use in accordance with the procedures described in detail herein.

In proceeding in accordance with the above, a compound is obtained which may be generically and diagrammatically illustrated by the following formula:



In further detail, the formula for the compound cellulose acetate dimethyl acetate is illustrated as follows:



In the formulas above it will be noted that the structure (branched line) on the left diagrammatically illustrates a cellulose molecule in which there would of course be a large number of repeating units. Certain of the hydroxyl groups of the cellulose are acetylated and certain others are aminoacetylated. In the foregoing formulas, while an acyl radical followed by a hydroxyl, followed by the aminoacyl has been shown, this is merely diagrammatic as there may be other arrangements within the molecule. The structure of cellulose is quite complex. Hence it is not desired to be bound by any particular internal molecular arrangement or configuration. It is sufficient to indicate the constituents making up the chemical compound and the minimum amount of nitrogen which it is preferred be present. As described above, the amino-acetylation is such that the aminoacyl compound contains more than 1½% nitrogen.

For convenience and brevity of reference in the further description we may refer to the aforementioned cellulose acetate diamino compounds as CADA. This acid soluble CADA material may be applied directly to film or sheeting from a solvent solution thereof. The resultant layer or coating after evaporating the solvent may be used as is or may be dyed or otherwise treated to obtain a special antihalation backing. However, in most instances we would prefer to incorporate into the CADA material various dyes, pigments and/or conducting agents for various purposes as will be apparent from the further description. For example, we have found that our CADA material may be milled with color pigments and also some conductive carbon milled in to produce a very useful antihalation layer and a layer which also affords good antistatic protection.

In the present invention we determined the antistatic protection afforded by a layer by measuring the surface electrical resistivity of the layer. If this measurement indicates a value of less than 1.0×10^{10} ohms per sq. cm.

(as compared to the value of greater than 1.0×10^{14} ohms on untreated film base) then satisfactory antistatic protection is indicated.

In further detail, the method and apparatus used in measuring antistatic properties of layers is as follows:

The value is measured by a surface electrical resistance measuring apparatus. This apparatus is built around a megohmmeter type 1020, manufactured by the Freed Transformer Company, New York, and it is designed to operate within a resistance range of 10^6 to 10^{12} , which is indicated by the position of the sensitivity selector switch on the megohmmeter. The electrodes used for this test consist of two steel plates 10 cm. in length and 0.5 cm. apart. Surface resistivity is defined as follows:

$$R = \rho \frac{W}{L}$$

R = True resistance measured on the megohmmeter

ρ = Surface resistivity measured in ohms

W = Distance between electrodes (0.5 cm.)

L = Length of electrodes in contact with the sample (10 cm.)

Hence, for the apparatus described, the surface resistivity of any sample can be determined by multiplying the true resistivity, measured on the instrument, by a factor of 20.

In use the sample whose surface resistivity is to be determined is held in contact with the aforementioned electrodes by a spring loaded metal bar. A 500 volt direct current charge is fed into the apparatus and the reading on the megohmmeter together with the sensitivity factor are noted. This figure is then multiplied by 20 to give the surface resistivity of the sample.

Further understanding of our invention will be had from a consideration of the following examples which are set forth primarily to illustrate certain of our preferred embodiments of the present invention.

Example I

In this example the particular CADA compound, N,N-diethylamino acetate, was milled with carbon particles (known as Statex, Southern Carbon Company, furnace carbon black) in the ratio of about 60 parts of the CADA to 40 parts of the carbon. After milling the ingredients together, a portion of the grind was incorporated in solvent to provide a coating composition of the following formula:

3.2% grind
55.0% ethylene chloride
41.8% methanol

This coating solution was applied to one surface of cellulose acetate film base by conventional coating procedure, then drying the coated film and rolling up the product. The resultant CADA layer on the film was of a thickness of between 1.2 and 12.0 microns. Test portions of the finished coated film were then tested both for optical density which was 1.5 and for resistivity which was less than 1×10^{10} ohms per sq. cm.

This film base carrying this CADA backing was further subjected to various operations such as emulsion coating and immersion in processing solutions, and the CADA backing examined after the various operations. In no instance did the backing show detachment.

A section of the film which had been emulsion coated, exposed and processed was then immersed with agitation for 10 seconds in dilute acid (0.5 to 1.0% glacial acetic acid in distilled water). The backing came off without flaking, and the support was free from stain and specks.

Also, in accordance with this example another run was made using the same grind but a different solvent to give the following coating composition:

4% grind
65% acetone
31% methanol

The resultant backed film product was separated into separate strips which were tested as just indicated. Here again the optical density was 1.5 and the resistivity less than 1×10^{10} ohms per sq. cm.

Another composition was made up using milled CADA which was free of any carbon, but was dissolved in an acetone-methanol solvent. Film base was coated therewith to give plain, unpigmented backing. This backing was tested for adherence and found to adhere satisfactorily even though the backed film base was subjected to various developing solutions and other types of photographic solutions.

Example II

In accordance with this example, 4% of the CADA material in this example was cellulose acetate N,N-diethylamino acetate) in a 75% acetone, 21% methanol solution, was applied to standard cellulose acetate film support. The solvent was evaporated to leave a thin backing by conventional procedure. This film support thus backed with the CADA was then immersed in a solution of the following composition:

2% nigrosine spirit jet (aniline black dye)
1% aerosol AY (wetting agent of dicarboxylic acid ester type—American Cyanamid Co.)
25% methanol
72% ethanol

After suitably drying the dyed film to permit the evaporation of the methanol-ethanol solvent which had been used for the dye, there was obtained a film product having an excellent antihalation backing. Various test strips of this backed film product with the instant antihalation backing were subjected to different processing solutions and the backed film reexamined. In all instances it was found that the backing withstood the processing solutions and exhibited no tendency to peel from the film base. The test strips were then treated in a mild acetic acid solution with the result that the antihalation backing was readily removed leaving a clean film base surface.

In further runs under the present example, the nigrosine dye was replaced with an antistatic material known as Daxad 11 (polymerized sodium salts of alkyl aryl sulfonic acids—from Dewey and Almy Chemical Co.). It was found that this antistatic material was well carried in the CADA to provide a good antistatic backing on the film base.

In another run under this example, β -methacryloxyethyl-diethylmethyl ammonium methylsulfate was incorporated in the above-described CADA-acetone-methanol solution and standard cellulose acetate film base coated therewith. The resultant backing on the film not only adhered satisfactorily, but exhibited a surface resistivity less than 1×10^{10} ohms per sq. cm.

In another run under this example, butyl amine salt of cellulose acetate sulfate was incorporated in the above-described CADA-acetone-methanol solution and standard cellulose acetate film base coated therewith. The resultant backing on the film not only adhered satisfactorily, but exhibited a surface resistivity less than 1×10^{10} ohms per sq. cm.

In a further run under this example the backings containing additives Daxad 11, β -methacryloxyethyl-diethylmethyl ammonium methylsulfate, and butyl amine salt of cellulose acetate sulfate, just mentioned, were immersed in the above-described nigrosine dye solution. In each case this resulted in a backed film performing a dual function. That is, the backed film not only exhibited antihalation properties, but also exhibited antistatic properties. This backed film exhibiting these dual properties was then tested in various processing solutions and the adherence of the backing inspected. In all instances the backing withstood the processing solutions without indication of separation. However, the back-

ings were readily removable in a weak acetic acid solution.

Example III

In accordance with this example the coating applied to film base had the following formula:

1.7% nigrosine spirit jet
2.1% β -methacryloxyethyl-diethylmethyl ammonium methylsulfate
1.9% CADA (cellulose acetate N,N-diethylamino acetate)
0.3% aerosol AY
77.0% acetone
17.0% methanol

The layer dispersed on film base in this example was between 1.2 and 12.0 microns in thickness. The resultant backed film not only exhibited good antihalation protection but likewise measured a resistivity of less than 1×10^{10} ohms per sq. cm., thereby exhibiting satisfactory antistatic performance. Tests of the type referred to in the preceding examples indicated satisfactory adherence of this backing in various photographic processing solutions as well as removability in a weak acid solution.

Example IV

In accordance with this example, a standard roll of cellulose acetate film base was first backed with a backing solution of 1% butyl amine salt of cellulose acetate sulfate, 1% sodium acetate from a 70% acetone, 28% methanol solvent. In other words the film base was first backed by conventional procedure with backing which has heretofore been used in the art.

This first backing was then overcoated with a backing in accordance with the present invention. That is, the first-mentioned layer was then overcoated with a coating deposited from the following formula:

2% CADA (cellulose acetate N,N-diethylamino acetate),
75% acetone
23% methanol

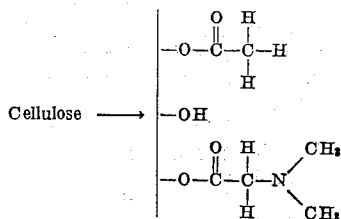
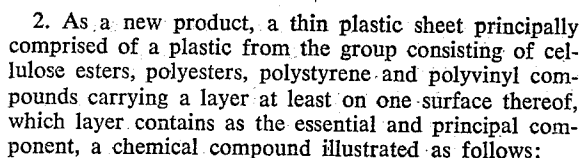
The finished product was measured for surface resistivity and a value of less than $.2 \times 10^{10}$ ohms per sq. cm. obtained, which was regarded as quite satisfactory particularly in the light of the additional advantages that were obtained. It was found that the second coat (overcoat) in accordance with the present invention quite effectively prevented softening of the first coat in high humidity and other such conditions which prevail in manufacturing operations such as emulsion coating. That is, the overcoat in accordance with the present invention permitted successful and practical utilization of the use of a first coat as above described under conditions where problems of adherence would arise in the event the overcoat in accordance with the present invention had not been employed.

Other runs in accordance with this example where the CADA coating is used as an overcoating were made. That is, runs were made where the overcoat was applied over a sensitometrically active backing. It was found that the overcoat in accordance with the present invention not only adhered satisfactorily, but prevented fogging of the emulsion when it was rolled against a backing that was sensitometrically active.

It can be seen from the foregoing examples that we have provided a new coating or backing material which may be utilized in various manners. That is, it may be used as a coating per se. This coating may be subsequently dyed or otherwise treated in several ways. Or, CADA coating may be used as a vehicle for various antistatic and dye materials. Also, our coating may be used as an overcoating on various coatings to protect such coatings so that the dual coated film product may be subjected to various manufacturing and processing operations.

While in the above examples we have referred to the application of our new CADA backing to cellulose acetate film base, which film base in general had either a

1. As a new product a thin plastic sheet principally comprised of a plastic from the group consisting of cellulose esters, polyesters, polystyrene and polyvinyl compounds carrying a layer at least on one surface thereof, which layer contains as the essential and principal component, a chemical compound illustrated by the following general formula:



9. The method of manufacturing a film product which comprises obtaining cellulose acetate film base material

and applying to at least one surface of said film material a composition made up of cellulose acetate N,N-dialkylamino acetate, an antihalation dye, an antistatic material and solvent which will substantially dissolve the aforementioned ingredients and cause them to attach to the film base, and evaporating off said solvent to leave a coating of the first-mentioned ingredients.

10. As an article of manufacture, a cellulose ester film base carrying on at least one surface a layer which is thinner than the thickness of said film base, said layer being principally comprised of a compound from the group consisting of cellulose acetate N,N-dimethylamino acetate, cellulose acetate N,N-diethylamino acetate, cel-

lulose acetate N,N-dipropylamino acetate, cellulose acetate morpholino acetate, cellulose acetate butyrate N,N-diethylamino acetate, and ethyl cellulose N,N-diethylamino acetate, and said layer also having incorporated therein a content of carbon particles.

References Cited in the file of this patent

UNITED STATES PATENTS

10 2,072,870 Dreyfus ----- Mar. 9, 1937

FOREIGN PATENTS

713,386 Great Britain ----- Aug. 11, 1954