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PHOTOGRAPHIC FILM WITH ANTISTATIC LAYER

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Fig. 1

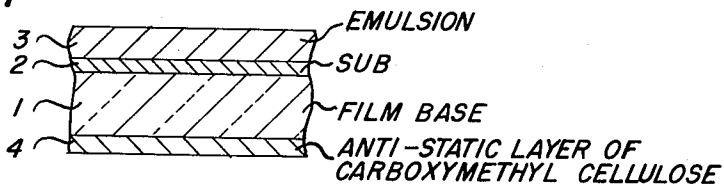


Fig. 2

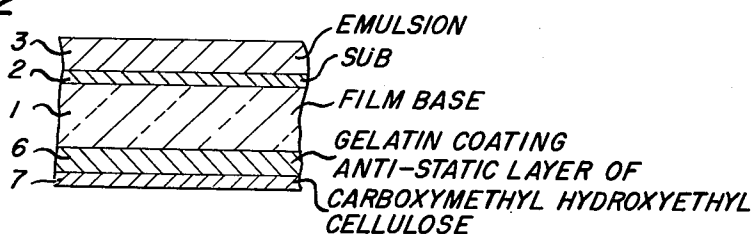
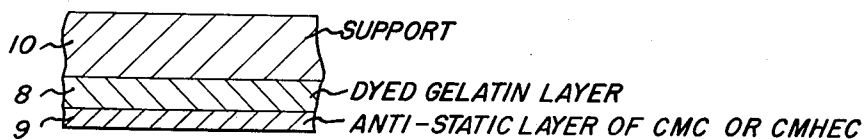


Fig. 3



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## PHOTOGRAPHIC FILM WITH ANTISTATIC LAYER

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This invention relates to the treatment of film, sheeting and the like web-form of article to provide protection against static. More particularly, this invention concerns a treating composition, a method for treating photographic film products as well as the improved film products resulting from the aforesaid treatment, which film products carry an improved antistatic layer.

It has been known in general for many years that the motivating, handling, winding, unwinding and the like operations when applied to webbed materials such as film may cause the formation of static. The problem of static in the photographic industry where the film carries a light-sensitive layer is well known and presents additional problems in that a static discharge can damage the emulsion carried on the film.

In addition, photographic film presents particular problems for several reasons. For example, film base being frequently comprised of a relatively non-porous material may present problems of finding antistatic layers that will adhere thereto in the desired manner. Also, the treating agent not only should accomplish the result of reducing the effect of the static but on the other hand the antistatic layer should not adversely affect the light-sensitive emulsion which is carried on the film and with which the antistatic layer may come in contact due to the winding of the film product.

Many solutions to the various types of static problems have already been proposed in the prior art. One usual way of treating films and sheets to reduce static is to apply a layer to the film or sheet known as an antistatic layer. In many instances such layers which have previously been used are binary or ternary systems. That is, the web to be treated against static is coated with combinations comprising gelatin and an ionic material. Also more complex combinations have been used comprising gelatin-polymeric component and inorganic salt. Many other materials and methods of application have been proposed.

Although a number of the prior art antistatic layers have merit in reducing or otherwise minimizing the development of a static charge, as mentioned, many of these layers have involved a ternary system or the like. Although the prior art procedures have been quite effective with the film bases and emulsions heretofore in use, such layers may not be entirely satisfactory with presently used components. That is, at the present time different type of film bases may be used than formerly. Likewise, the photographic film may carry more sensitive emulsions thereby presenting the problem of greater susceptibility to static.

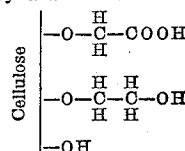
Accordingly, it is believed apparent that the development of simpler, more effective antistatic treatments for film and sheets of the class referred to represents a highly desirable result. After extensive investigation we have discovered what we consider is a more effective antistatic treatment for products of the class described.

This invention has for one object to provide a new procedure for treating films, sheets and the like articles to protect them against static. A particular object is to provide a photographic film product comprised of a flexible base which carries a light sensitive emulsion, which base also carries an improved antistatic layer. Still another object is to provide an antistatic layer for use on

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film surfaces which is more effective and economical than antistatic layers heretofore employed. Another object is to provide an antistatic layer of the class indicated which is effective on various type film bases which carry various types of light-sensitive emulsions. Still another object is to provide an antistatic layer which gives protection to photographic film which carries relatively high speed emulsions. Another object is to provide a method of applying such type layers to film articles in a relatively simple manner. A still further object is to provide an antistatic layer on film which will adhere to the film for a certain period but which is susceptible of removal during film processing. Other objects will appear hereinafter.

In the broader aspects of our invention we have found that certain cellulosic derivatives, alone and without their mixture into ternary systems or the like, may be applied to film in a very simple, inexpensive manner to obtain on the film a very effective antistatic layer. The cellulose derivatives employed for the antistatic layer of the present invention are carboxymethyl cellulose and carboxymethyl hydroxyethyl cellulose, which materials will be referred to hereinafter for convenience as CMC and CMHEC. Such type of cellulose derivatives may be generally illustrated by a formula as follows:



In the above formula a simple line structure has been employed for designating the cellulose molecule, which molecule has three hydroxyl groups. The hydrogen atoms of one or more of such hydroxyl groups may be replaced with the carboxymethyl radical as shown in the upper position in the formula. Or the replacement may be by the hydroxyethyl radical as shown in the middle position. The last position in the above formula is shown as the unreplaced hydroxy group. For the derivative carboxymethyl cellulose, the hydrogen atoms of the hydroxy groups replaced would have been replaced by the carboxymethyl radical,  $\text{—CH}_2\text{—COOH}$ . For CMHEC, both types of radical would be present as generically depicted in the above formula. We generally prefer to use cellulose derivatives in which substantially all of the hydroxyl groups have been replaced by one or both of the aforesaid radicals.

Such type of cellulose derivative compounds as above discussed are known compounds and may be obtained commercially. For example, the publication Industrial and Engineering Chemistry, vol. 29, No. 1, page 114 et seq. describes the production of various hydroxy alkyl ethers of cellulose of the type discussed above. Industrial and Engineering Chemistry, vol. 37, No. 10, page 943 et seq. discusses carboxymethyl cellulose. Accordingly, further detailed description concerning the general nature of the cellulose derivatives which we employ in the instant invention appears to be unnecessary. We would point out, however, that we prefer to use a type of CMC designated as No. 120 and which may be obtained from the Hercules Powder Company. Such type of CMC is further characterized by the following properties:

CMC 120 so designated because its average degree of substitution is approximately 1.20 or in other words 40% of the hydrogens of the hydroxyl groups of the cellulose have been replaced by carboxymethyl, is a relatively neutral salt readily soluble in water. Its normal degree of substitution range is 1.20–1.40 (a completely reacted product would have a substitution of 3.0). As may be noted from U.S. Patent No. 2,824,092, the degree of sub-

stitution indicates the average number of carboxy methyl groups substituted in each anhydride glucose unit of the molecule. A 2 percent aqueous solution of CMC 120 has a viscosity range of 400-800 centipoises at 25° C. CMC 70 referred to in Example III is a carboxymethyl cellulose having an average degree of substitution of approximately 0.70 or in other words 23⅓% of the hydrogens of the hydroxyl groups of the cellulose have been substituted.

As to CMHEC, we prefer to utilize the compound identified as No. 37 and likewise obtained from the Hercules Powder Company. This particular type of material is further identifiable by having the following properties:

CMHEC 37, chemically, is the sodium salt of carboxymethyl hydroxyethyl cellulose. CMHEC has an average substitution of 0.3 carboxymethyl groups and 0.7 hydroxyethyl groups. This material thus has an average substitution of approximately 1.0 or in other words 33⅓% of the hydrogens of the hydroxyl groups of the cellulose have been replaced by carboxymethyl and hydroxyethyl. Its viscosity range is 15-100 centipoises in 2 percent aqueous solution and at 25° C. CMHEC 43 mentioned in column 5 as being useful, has an average substitution of 0.4 carboxymethyl and 0.3 hydroxyethyl groups or in other words an average degree of substitution of approximately 0.7, which is equivalent to substitution of 23⅓% of the hydrogens of the hydroxyl groups of the cellulose by carboxymethyl and hydroxyethyl.

Although we prefer the types of material just described, in the broader aspects of our invention other cellulosic derivatives of the same general type may be used provided they from aqueous solutions and are suitable for coating.

Compounds of the above type may be readily dissolved in water to form solutions of a concentration of 1-5%, for example. However, for most purposes we have found that a 1-2% solution is quite satisfactory. The viscosity ranges we have described previously are the preferred ones. Higher viscosity coatings could probably be made, but at these higher viscosities they become cumbersome and much more difficult to work with.

Although as above discussed we use the carboxymethyl cellulose derivative as the principal antistatic agent and do not form binary or ternary systems, this does not exclude the use of matting agents and certain additives of that type. As will be described hereinafter, in many instances we prefer to include certain solid derivatives for breaking up the uniformity and smoothness of our antistatic coating in order that the film product will not have a tendency to ferrotype. Also these matting agents have been found to minimize unwinding static by reducing points of contact.

From the foregoing description it will be observed that we have discovered that a relatively simple aqueous solution of a carboxymethyl cellulose derivative without salts or other antistatic agent additives may be applied to film materials as an antistatic layer. We have found that such antistatic layer gives better static protection than the more complex antistatic layers heretofore used in the prior art.

Aqueous solutions in accordance with our invention and as above described may be coated onto various types of films and sheets by any convenient method. That is, our antistatic layer can be applied by a roll applicator or from a coating hopper adapted to apply a very thin layer. The exact manner and equipment used for applying the antistatic layer of the present invention to the web material is not a limitation on the invention.

For a further understanding of this invention reference is made to the attached drawing forming a part of the present application. In this drawing the several figures shown are sectional views on the large scale of a film type product carrying the antistatic layer of the present invention. The various figures are thought to be readily understandable from the legends appearing thereon but a few brief sentences of description are now set forth.

Referring to FIG. 1 there is shown a section of a somewhat standard photographic film product. This product is comprised of film base 1. The film base may be the older film base material exemplified by nitrate film or it may comprise more recent type of film base. For example, we prefer a film base of cellulose acetate having an acetyl content within the range of approximately 42-44%. The film base may also be of polyester material as will be described hereinafter. In some of the examples such film base is subbed on one side as indicated at 2 with a sub compatible with the particular film base material used. Positioned over this sub is one or more layers of light-sensitive emulsion as indicated at 3.

The opposite side of the film base carries an antistatic layer 4 of carboxy methyl cellulose or of carboxy methyl hydroxyethyl cellulose in accordance with the present invention. The antistatic layers of FIGURE 1 were coated over sub-layers similar to those used for the emulsion side.

Referring to FIG. 2, the film product shown is generally similar to that described in connection with FIG. 1 excepting that the film base 1 carries the gelatin coating 6. The antistatic layer 7 of the present invention is comprised of a carboxymethyl hydroxyethyl derivative and is overcoated over this gelatin layer.

FIG. 3 illustrates a dyed gelatin film at 8 which has CMC or CMHEC antistatic layers 9 on one side of the gelatin film and support 10 on the other side.

The new antistatic layer in accordance with the present invention may be relatively thin and yet give excellent protection. That is, the amount of 25 mg.-200 mg. of the cellulose derivative per square foot of film when coated provides an antistatic layer of satisfactory thickness. Higher amounts of the cellulose derivative may be used. However, added thickness is not considered as compensating for the additional expense and delay of coating. In general, therefore, we would prefer that our antistatic layer would contain less than 200 mg. per square foot but be sufficiently thick to provide a substantially continuous layer on the film being coated with our antistatic material.

In addition to the effective static protection given by the layers of the present invention, our layers have further advantages in that they may be removed in photographic processing solutions. That is, after the antistatic layer has performed its function and the photographic product has been exposed, processed, etc., the antistatic layer is absent from the finished photographic negative.

For a more complete understanding of our invention, reference will be made to the following examples illustrating certain preferred embodiments thereof.

#### Example I

In accordance with this example a 1.5% aqueous solution of the cellulose derivative referred to above as CMC 120 was made up. This CMC solution may be accomplished by adding the dry powder gradually to water, or by first wetting the powder with alcohol (ethyl or methyl) and then adding the compound to water. The latter method avoids clumping of the powder in water. The material is then mechanically stirred until all of the CMC 120 appears to be in solution. The solution is then filtered before using. In addition there was also incorporated into the solution approximately 10 cc. of saponin for every 100 ml. of solution as a coating aid. The saponin solution was prepared by incorporating 153.4 gms. of saponin in 1000 cc. of distilled water with moderate stirring to accomplish the solution. Since this is a well-known coating aid further description thereof appears to be unnecessary.

The 1.5% solution thus prepared was coated onto the back of a subbed film base such as generally illustrated in FIG. 1. The coating was accomplished by means of a known extrusion hopper type of apparatus at a rate of 150 mg. of CMC per square foot of the film base.

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## Example II

In accordance with this example 1.5% aqueous CMC solution as just described was coated with similar coating apparatus onto a film product containing a dyed gelatin pelloid in its make-up such as generally illustrated in FIG. 3.

## Example III

In accordance with this example a 1.5% solution as described in the preceding examples was coated over a clear gelatin pelloid by coating procedure as already described.

The sheet products of the preceding examples, which products carried an antistatic layer, in accordance with the present invention were tested by a test procedure to be described hereinafter. The results of these tests are as follows:

| Results:                         | Surface resistivity at<br>50% RH ( $\times 10^{10}$ ohms) |
|----------------------------------|-----------------------------------------------------------|
| Subbed film support              | 10,000                                                    |
| Dyed Gelatin Pelloid             | 21                                                        |
| Clear Gelatin Pelloid            | 143                                                       |
| CMC 120 on subbed film support   | .074                                                      |
| CMC 120 on dyed gelatin pelloid  | .049                                                      |
| CMC 120 on clear gelatin pelloid | .17                                                       |
| CMC 70 on subbed film support    | .12                                                       |
| CMC 70 on dyed gelatin pelloid   | .092                                                      |
| CMC 70 on clear gelatin pelloid  | .23                                                       |

It will be observed from the above table that the resistivity of the various film base and pelloids was materially reduced as a result of the application of the antistatic layer in accordance with the present invention.

## Example IV

In accordance with this example an aqueous coating solution of the cellulose derivative CMHEC 37 was made up. This was accomplished by first dissolving 0.5 gm. of the CMHEC 37 in 100 cc. of distilled water with moderate agitation. As a coating aid 1 cc. of saponin solution was added. This coating aid had been made up previously by dissolving 153.4 gm. of the saponin in 1000 cc. of distilled water. The cellulose derivative containing solution in accordance with the present invention was then applied as an antistatic layer over a dyed gelatin pelloid at the rate of 50 mg. of the CMHEC per square foot of the gelatin pelloid.

## Example V

In accordance with this example a coating solution was made up of about 2 gm. of CMHEC 43 (viscosity 90 cps.) dissolved in 100 cc. of water. 1 cc. of a coating aid comprising a saponin solution as described in the preceding example was incorporated. The coating solution of the present invention was then applied as an antistatic layer onto film support which carried a clear gelatin pelloid and over such pelloid layer.

A similar coating solution was also applied over a subbed film support carrying a dyed pelloid layer. The rate of coating was approximately 200 mg. of the CMHEC per square foot of the gelatin pelloid.

The film products of Examples IV and V were tested for surface resistivity. The results of these tests are set forth below in the following table:

| Results:                                     | Surface resistivity at<br>50% RH ( $\times 10^{10}$ ohms) |
|----------------------------------------------|-----------------------------------------------------------|
| Subbed film support                          | 10,000                                                    |
| Dyed Gelatin Pelloid                         | 21                                                        |
| Clear Gelatin Pelloid                        | 143                                                       |
| CMHEC 37 on clear gelatin pelloid            | 3.3                                                       |
| Tamol P in CMHEC 37 on clear gelatin pelloid | 1.8                                                       |
| CMHEC 43 90 cps. on subbed support           | 1.8                                                       |
| CMHEC 43 90 cps. on dyed gelatin pelloid     | .91                                                       |
| CMHEC 43 90 cps. on clear gelatin pelloid    | 3.2                                                       |
| CMHEC 43 27 cps. on subbed support           | 1.9                                                       |
| CMHEC 43 27 cps. on dyed gelatin pelloid     | .89                                                       |
| CMHEC 43 27 cps. on clear gelatin pelloid    | 3.1                                                       |

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It will be observed that in all instances the antistatic layer in accordance with the present invention materially reduced the resistivity of the film support or pelloid.

## Example VI

In accordance with this example a film base comprised of cellulose acetate of an acetyl content between 42 and 44% was the base upon which the antistatic layer of the present invention was employed. The antistatic layer comprised an aqueous CMC 120 solution of a concentration within the range of 1-2%. In addition the CMC antistatic solution of the present invention contained zinc carbonate as a matting agent (of the order of 1% based on the weight of the coating solution).

The following table shows a comparison between the film base used as a check and the film base which was coated with the CMC and zinc carbonate of the present invention:

|                                                              | check <sup>1</sup> | CMC 120+<br>ZnCO <sub>3</sub> <sup>2</sup> |
|--------------------------------------------------------------|--------------------|--------------------------------------------|
| 4 min. chagemeter value e.s.u./cm. at 40% RH.                | +13                | 0                                          |
| Backing resistivity $\times 10^{10}$ ohms                    |                    | 0.079                                      |
| Stock roll potential (volts) on film as received.            | +500               | +10                                        |
| Stock roll potential (volts) on film incubated 1 day 120° F. | -9,000             | -5                                         |

<sup>1</sup> No pelloid on the support.

<sup>2</sup> CMC 120+ZnCO<sub>3</sub> coated as a pelloid on the support.

In the above table, by chagemeter value, we mean the equilibrium value obtained at the end of 4 minutes. This value is obtained in electrostatic units per centimeter length.

## Example VII

In accordance with this example the effectiveness of the antistatic layers of the present invention were tested by a practical camera test at 15% relative humidity. That is, a film product was made up of the same general type as illustrated in FIG. 1. The film base carried on one side a relatively high speed negative emulsion. On the other side of the film base was positioned the antistatic layer of the present invention essentially comprised of CMC 120 type coated on the film base at the rate of 150 mg. per square foot.

In another run the antistatic layer was comprised of CMC plus zinc carbonate coated over a gelatin antihalation layer which was carried on the film base.

The practical camera test briefly comprised the following: The films were conditioned at 15 percent RH and at 70° F. for 3 days, and then exposed in a camera under similar conditions of temperature and relative humidity. Exposures were made on alternate frames of the film. The film was then developed in an elon-hydroquinone developer. After developing, fixing, and washing, the film was examined for static markings. In each case, four 20-exposure rolls of film were subjected to tests in each of the test cameras.

An examination of the processed film from these tests indicated that any static markings had been effectively eliminated by the antistatic layers of the present invention. This was observable because control film which did not have an antistatic backing in accordance with the present invention showed static marking in the majority of the frames.

## Example VIII

In this example the coating and testing was substantially similar to the preceding example. That is, the antistatic layer coated was comprised of CMC and zinc carbonate. However, the film base involved was a material known in the trade as polyester film. This is a material identified chemically as polyethylene terephthalate. This particular film base carried a medium speed negative emulsion on one side and the side opposite the emulsion carried an antistatic layer of the present invention coated at the rate of 100-150 mg. per square foot of the poly-

ester film base onto an antihalation gelatin pelloid. Here again, the test, as compared with control film indicated that the present invention effectively eliminated any static markings.

It is thought that it may be seen from the foregoing that our new antistatic layer may be applied to various types of film base. These may comprise cellulose acetate or polyester supports. In all instances suitable protection against static was procured. Although in a number of instances we have described the use of an antistatic layer that is substantially entirely composed of the carboxy cellulose derivative, we contemplate the presence of small amounts of certain other materials. For example, matting agents such as the zinc carbonate mentioned above may be included to the extent of 50% based on weight of dry antistatic material. In addition to the carbonate, alkali soluble cellulose acetate phthalate may be readily dispersed as a matting agent in the layers of the present invention. Therefore, we contemplate the use of matting agents comprised of materials which may be dispersed in small amounts throughout our antistatic layer.

We have described the use of saponin as a coating aid inasmuch as this is a material frequently used in the photographic industry for such purposes. However, in place of or supplemental to such coating aid we may use various other types of coating aid. The aids are used in a relatively small quantity merely sufficient to facilitate the coating operation. We have found that in conjunction with the use of CMHEC that a material obtained commercially as Tamol P is a useful additive. Tamol P is the sodium salt of the condensation product of naphthalene sulfonic acid and formaldehyde. Although small amounts of certain additives as just illustrated may be incorporated in our new antistatic layer, in general we prefer not to dilute our antistatic layer to any great extent. We have found that dilution, particularly with substantial amounts of other vehicles such as gelatin, substantially reduces the conductance of the antistatic layer.

Our invention is not only useful with photographic films which carry light-sensitive emulsions of moderate sensitivity but also our invention is useful where the film carries an emulsion which may be referred to as a high speed type of emulsion. Therefore, the particular emulsion carried on the photographic product of this invention is not a limitation and extensive description with respect to such emulsion appears unnecessary. It is thought sufficient to indicate that the emulsions carried by the film product of the present invention would usually be a silver halide type. Different sensitivities of emulsion may be obtained in a number of ways as may be noted by reference to the rather extensive description contained in Photographic Journal of May 1939, at page 330 et seq. In connection with certain of the examples herein we have shown that our new antistatic layer changes the surface resistivity (at some particular RH) from greater than  $10,000 \times 10^{10}$  ohms to a much lower value. This type measure of resistivity is a convenient way for ascertaining the effectiveness of layers for antistatic purposes. Values below  $1 \times 10^{10}$  ohms indicates that the antistatic properties of the film thus treated will be quite satisfactory. Surface Resistivity is resistance, measured in ohms, when a voltage is applied between two electrodes at a specified distance apart. It is measured in ohms per square (either centimeters or inches). This value may be measured by surface electrical resistance measuring apparatus. Such apparatus may be built around a Megometer type unit manufactured by the Freed Transformer Company, New York. The apparatus comprises two parallel electrodes on the film at fixed relative humidity conditions. These electrodes are long compared to the distance between them so as to avoid end effects. The observed resistance reading is divided by the distance between the electrodes and multiplied by the length to obtain the surface resistivity. A high voltage direct current charge is fed into the apparatus.

The particular apparatus used in measuring resistivity, however, is not a limitation on the present invention.

It is believed apparent from the foregoing that we have provided a relatively simple and economical way of securing static protection on various types of film products.

We claim:

1. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of cellulose derivative selected from the group consisting of the low viscosity carboxymethyl celluloses having an average degree of substitution within the range of approximately  $23\frac{1}{3}\%$  to approximately 40%, the low viscosity carboxymethyl hydroxyethyl celluloses having an average degree of substitution within the range of approximately  $23\frac{1}{3}\%$  to approximately  $33\frac{1}{3}\%$  and mixtures thereof with up to 50% of matting agent selected from the group consisting of zinc carbonate and alkali soluble cellulose acetate phthalate, and coating aid selected from the group consisting of saponin and the sodium salt of the condensation product of naphthalene sulfonic acid, and formaldehyde.

2. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl cellulose having an average degree of substitution within the range of approximately  $23\frac{1}{3}\%$  to approximately 40% and saponin coating aid.

3. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl cellulose having an average degree of substitution of approximately 40% and saponin coating aid.

4. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl cellulose having an average degree of substitution of approximately  $23\frac{1}{3}\%$  and saponin coating aid.

5. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl hydroxyethyl cellulose having an average degree of substitution of approximately  $33\frac{1}{3}\%$  and as the coating aid therein the sodium salt of the condensation product of naphthalene sulfonic acid, and formaldehyde.

6. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl hydroxyethyl cellulose having an average degree of substitution of approximately  $33\frac{1}{3}\%$  and saponin coating aid.

7. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl hydroxyethyl cellulose having an average degree of substitution of approximately  $23\frac{1}{3}\%$  and saponin coating aid.

8. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of saponin coating aid and low viscosity carboxymethyl cellulose having an average degree of substitution within the range of approximately  $23\frac{1}{3}\%$  to approximately 40%, containing up to 50% of zinc carbonate.

9. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of saponin coating aid and low viscosity carboxymethyl cellulose having an average degree of substitution within the range of approximately  $23\frac{1}{3}\%$  to approximately 40% containing up to 50% of alkali soluble cellulose acetate phthalate.

10. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl hydroxyethyl cellulose having an average degree of substitution within the range of approximately 23⅓% to approximately 33⅓% containing up to 50% of zinc carbonate and saponin coating aid.

11. A photographic product comprising a support carrying on one side a photographic emulsion layer and on the opposite side an anti-static layer consisting of low viscosity carboxymethyl hydroxyethyl cellulose having an average degree of substitution within the range of approximately 23⅓% to approximately 33⅓% contain-

ing up to 50% of alkali soluble cellulose acetate phthalate.

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