

United States Patent

Mackey

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[54] **ANTIHALATION PHOTOGRAPHIC
MEDIA AND METHOD OF
PREPARATION**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 835,890, June 12, 1969, abandoned, which is a continuation of Ser. No. 480,140, Aug. 16, 1965, abandoned.

[52] U.S. Cl.117/33.3, 96/84

[51] Int. Cl.G03c 1/84

[58] Field of Search96/84; 117/33.3; 252/300

[56]

References Cited

UNITED STATES PATENTS

1,990,143	2/1935	Snow	117/33.3
2,095,018	10/1937	Wilmanns et al.	96/84
3,026,202	3/1962	Konx et al.	96/94
3,415,649	12/1968	Nishio et al.	96/94

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[57]

ABSTRACT

Preparation of antihalation layers by applying a gelatin coating containing a small amount of a manganous salt to a film base, and applying thereto an aqueous permanganate rinse containing an anionic surfactant which is nonreactive with the permanganate and is selected from the group consisting of the alkali metal salts of alkyl benzene sulfonic acids, and the alkali metal salts of polyfluoro- and perfluoro-aliphatic surfactants, having a sulfonic or carboxylic acid group.

5 Claims, No Drawings

ANTIHALATION PHOTOGRAPHIC MEDIA AND METHOD OF PREPARATION

This application is a continuation-in-part of my copending application Ser. No. 835,890 filed June 12, 1969, now abandoned, which in turn is a continuation of my application Ser. No. 480,140 filed Aug. 16, 1965 and now abandoned.

The present invention relates to improved antihalation media for photographic purposes and a method of preparing such. It has particular application to preparation of inert layers containing manganese dioxide of appropriate type for antihalation purposes.

In photography, particularly when bright objects are photographed, an undesirable phenomenon known as halation frequently occurs. A sort of secondary image or halo is formed which is due to reflection of light back into the emulsion from the rear of the film base or other support sheet. The density or intensity of the undesirable halo increases with exposure and also with the contrast but is reduced in proportion to the thickness and opacity or turbidity of the emulsion coating. Various remedies have been devised, probably the most successful being the placing of a light absorbing or antihalation layer on the base sheet to prevent reflection.

It has long been known that one or more layers of so-called pyrolusite is very effective as an antihalation material. This material consists of certain hydrated oxides of manganese, commonly obtained by causing potassium permanganate solution to act on gelatin of the emulsion to produce the pyrolusite in colloidal form. This material often has adverse effects on the quality of the gelatin and it has been suggested, as in U.S. Pat. No. 2,095,018 that thermal treatment of the pyrolusite, before incorporating in the gelatin, will destroy the higher hydrated components which are the most objectionable.

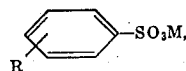
The technique of the prior art, including that of the patent just mentioned, has certain disadvantages, however. For example, in the technique of U.S. Pat. No. 2,095,018, the manganese dioxide pigment must be ground and redispersed. Even with intensive milling or grinding it is difficult or impossible to obtain the colloidal size particles often desired for high-quality photographic work. A so-called Harriman technique of using polyvinyl alcohol produces a product which tends to show a yellow residual stain, undesirable for most applications. The use of gelatin as the reducing agent for the permanganate produces a number of problems, such as embrittling the gel. This may be due either as a result of the reaction between gelatin and permanganate or to the production of excessive quantities of salts. The reaction itself is uncertain and difficult to control, resulting sometimes in production of a rubbery mass or the production of agglomerates of such particle size as to plug the filters in the equipment where emulsions are prepared and applied. Alternatively, if adjustments are made to eliminate these problems, the antihalation layer is often of inadequate density.

It is, therefore, a primary object of the present invention to prepare in effective antihalation layer which contains manganese dioxide as the light absorbing agent but which obviates the difficulties encountered above. A particular object is to provide a new and improved method for reducing potassium permanganate to manganese dioxide which avoids the problems associated with this reaction. Still a further object is to devise a novel and superior method of preparing an antihalation coating or layer for photographic media such as plates and films, etc.

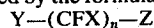
Stated in general terms, the objectives of this invention are achieved by preparing manganese dioxide or pyrolusite through the reduction of potassium permanganate which is applied as an aqueous rinse containing an anionic surfactant, which is nonreactive with the permanganate and is selected from the group consisting of the alkali metal salts of alkylbenzene sulfonic acids and the alkali metal salts of polyfluoro- and perfluoro-aliphatic surfactants having a sulfonic or carboxylic acid group, onto a coated clear gelatin layer, containing a small amount of a manganous salt, during the conventional coating operation. When so applied reaction takes place between the permanganate and the manganous salt with the

formation of manganese dioxide in the gelatin layer while avoiding the problems of manufacture mentioned heretofore.

This novel method of manufacture necessitates the use of certain surfactants to permit the permanganate rinse to be applied smoothly to the gelatin at high coating speeds. The surfactants which I have found to be suitable for use in practicing the present invention are (1) the alkali metal salts of alkylbenzene sulfonic acids of the formula



wherein R is an alkyl group of (either straight or branched chain) 10 to 20 carbon atoms, and M is ammonium or alkali metal, e.g., sodium or potassium. I particularly prefer the sodium and potassium salts of the commercially available dodecyl- and tridecylbenzene sulfonic acids which are essentially free of builders and other inorganic salts, such as Santomerse 3 and Santomerse 3 paste of Monsanto Chemical Co., or (2) the alkali metal or ammonium salts of polyfluoro- and perfluoro-aliphatic surfactants having a sulfonic or carboxylic acid group and characterized by the formula:



wherein:

Y is H, Cl or F (preferably F)

X is Cl or F (preferably F)

Z is a solubilizing group selected from the group consisting of $-\text{COOM}$, $-\text{SO}_3\text{M}$, $-\text{CO}-\text{NR}-(\text{CH}_2)_{n'}-\text{COOM}$ or $-\text{SO}_2-\text{NR}-(\text{CH}_2)_{n'}-\text{COOM}$

wherein:

R is alkyl of one to six carbon atoms,

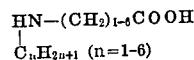
M is alkali metal or ammonium

n' is an integer of from 1 to 6 and n is an integer of from 4 to 20.

As examples of suitable perfluoro-alkyl carboxylic and sulfonic acids may be mentioned:



I particularly prefer the alkali metal salts of perfluoro-alkanoic acids of about six to 12 carbon atoms or mixtures of such acids, a number of such acids are described by Kanck and Diesslin, in Ind. Eng. Chem. 43,2332 (Oct. 1951) commercial products of this type are the ammonium salt of a mixture of C_4 to C_{10} perfluoro carboxylic acids, predominately the C_6 acid (wetting agent F-126, Minnesota Mining and Manufacturing Co.), and the potassium salt of a mixture of C_8 to C_{10} perfluoro carboxylic acids (Fluorochemical FC-98, Minnesota Mining and Manufacturing Co.). A number of suitable polyfluoro-alkanoic acids are disclosed in U.S. Pat. Nos. 2,559,630 and 2,904,515. The carbonamides and sulfonamides of the general formula given above can be prepared by reacting the acid chlorides of a polyfluoro- or perfluoro acid, such as those mentioned above, with sarcosine or other N-alkylaminoalkanoic acids of the formula:



The use of other types of surfactants, which are more commonly used as coating aids in the industry, have been found to be unsatisfactory for use in the process of the present invention since, inter alia, they react with the permanganate and form a precipitate. Typical types of surfactant which have been tried but found to be unsatisfactory are: saponin, sodium methyl oleyl taurate (Igepon), hydrolyzed protein condensates (Maypon), Miranols, Deriphats etc. In general, the polyoxyethylene surfactants, also of use as coating aids in the

industry, react at a much slower rate and are unsatisfactory for this reason. In addition, these produce unacceptable rinsing properties at high coating speeds—the rinse is repelled from the gel layer.

The composition of the clear gel layer which is rinsed is preferably formulated with agents normally used with those familiar in the art. These consist of a coating aid and hardener. According to this invention it is found that small amounts of (usually about 0.05 to 0.5 percent by weight based on the gelatin) of a manganous salt, such as manganous chloride, sulfate, nitrate or acetate, in the gelatin will insure a complete reaction of the permanganate rinse.

In practice, it is found that the clear gel layer containing suitable coating finals is applied from one coating station by normal air knife technique and while still wet and chilled is then rinsed at a second coating station with the permanganate solution containing the special surfactant. The rinse is also air knife applied. The coating then passes through the coating machine in a normal manner. This technique permits coating speeds up to the capacity of the coating machine.

As a specific illustration of this novel method of preparing an antihalation layer, the following example is cited. It will be understood, however, that variations may be made in the procedure without sacrificing the advantages of the invention.

EXAMPLE

A clear gelatin layer containing a wetting aid, such as saponin, and hardener, such as formaldehyde, and a small amount (about 0.01 percent by weight based on the gelatin) of manganous sulfate was applied from a coating pan to form a layer of sufficient thickness to provide curl properties which would be balanced by the emulsion coating on the opposite side of the film base. While still wet and chilled, this layer was passed on through the machine and rinsed with a solution comprised of:

Solution 1

Water	9.6 liters
KMnO ₄	300.0 g.
Santomerse 3 Paste	10.0 g.
	(dissolved in 100 cc. H ₂ O)
(Santomerse 3 Paste is an aqueous paste (75% active) of purified sodium dodecyl benzene sulfonate)	

OR

Solution 2

Water	8.0 liters
KMnO ₄	300.0 g.
Flurochemical FC-98	10.0 g.
	(dissolved in 2,000 cc. H ₂ O)
(Flurochemical FC-98 is the potassium salt of a mixture of perfluoro aliphatic acids of eight-10 carbon atoms, i.e., F(CF ₂) ₈₋₁₀ COOK)	

The solution was applied at coating speeds up to and over 60 f.p.m. The air pressure of the air knife was varied to accommodate for increased solution "pickup" and thereby control the amount of permanganate available for reaction with the gelatin. The rinsed layer was then passed through the machine and dried in the normal manner. Observation of the finished coating showed a brown antihalation layer suitable for photographic use.

If the rinse solution had been prepared with Saponin or Igepon or Deriphath or Maypon or similar coating aids normally useful for photographic use, the permanganate would react prematurely with these coating aids and form MnO₂ specks and clumps. When coated, these particles would deposit on the gelatin and form a rough layer which is unsuitable for photographic purposes.

It has also been observed that if the coating aid, i.e., the surfactant of the type specified above as useful, is omitted from the permanganate solution, the solution will not rinse the gel smoothly and evenly. Large unrinsed areas appear (repellent areas), and as coating speeds increase, the solution may only rinse on the gel in scattered droplike areas making the coating completely useless.

It is to be understood by those familiar with the art that the density requirements of the antihalation layer may vary according to the use. The antihalo density achieved by the present invention can readily be adjusted by at least two techniques: (1) adjustment of permanganate concentration up to limit of solubility; (2) alter the mechanics of coating by adjusting air pressure to permit varying amounts of the rinse to be available for the reaction or adjust machine speeds to vary rinse "pickup" and thereby control the amount available for the reaction.

In general terms, the antihalation layer comprises a manganese compound, preferably the dioxide, and preferably hydrated to a moderate degree, finely dispersed as a non-granular coating and so applied as to insure thorough coverage of the base support. The latter, especially when it is a film base, as is usually the case, necessarily has a highly reflective surface. To be effective, the antihalation layer must cover the base thoroughly and still be a thin layer, free from granules, rugosities, or roughness in general.

The use of the surfactant material, in sufficient proportions to insure complete and smooth coverage, is an essential feature, but the selected surfactant must not be reactive towards the manganese compound.

Generally speaking, a small amount of potassium permanganate is imbibed and mixed into the gelatin or other colloidal carrier or base layer containing a manganous salt and it reacts therewith to a sufficient extent to be converted to manganese dioxide. The preferred procedure is thereafter to wet this base coating with an aqueous solution of potassium permanganate which solution also contains the surfactant. In other words, part of the manganese compound is carried in the base coating—normally a very thin layer of gelatin or the like, and the remainder is imbibed into such layer from a separate and later application of permanganate.

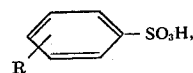
Obviously, more than one coating of the base gelatin or equivalent may be applied if desired. Also, the step of moistening the base coat with an aqueous solution permanganate and surfactant may be repeated if desired.

It will be apparent to those skilled in the art that a number of modifications may be made in the specific procedure outlined in the foregoing example. For instance, the coating technique may employ other conventional coating devices and procedures and other surfactants may be used, so long as they avoid the disadvantages mentioned above, such as causing premature reaction, or too extensive reaction, producing agglomerates, specks and granules, etc.

It is intended by the claims which follow to cover the above variations and such other modifications as would readily occur to those skilled in the art, including alternatives, and obvious equivalents, even though not expressly enumerated herein, as far as the state of the prior art properly permits.

I claim:

1. The method of producing a photographic antihalation layer which comprises applying to a film base, a thin layer of gelatin containing from about 0.05 to 0.5 percent by weight of a manganous salt, based on the quantity of gelatin, and thereafter applying to said gelatin layer an aqueous permanganate solution containing an anionic surfactant in an amount effective to cause uniform wetting of said gelatin layer, said anionic surfactant being selected from the group consisting of the alkali metal and ammonium salts of alkylbenzene sulfonic acids of the formula



wherein,

R is an alkyl group of 10 to 20 carbon atoms, and the alkali metal and ammonium salts of polyfluoro- and perfluoro-aliphatic surfactants having a sulfonic or carboxylic acid group and the having the formula



wherein,

Y is H, Cl or F.

X is Cl or F

z is $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{CO}-\text{NR}-(\text{CH}_2)_{n'}-\text{COOH}$ or $-\text{SO}_2-\text{NR}-(\text{CH}_2)_{n'}-\text{COOH}$ wherein, R is an alkyl group of one to six carbon atoms,

n' is an integer of from 1 to 6 and n is an integer of from 4 to

20.

2. The method as defined in claim 1 wherein the surfactant specified is an alkali metal salt of dodecylbenzene sulfonic acid.

3. The method as defined in claim 2 wherein the surfactant specified is sodium dodecylbenzene sulfonate.

4. The method as defined in claim 1 wherein the surfactant specified is an ammonium or alkali metal salt of a perfluoro-alkanoic acid of about six to about 12 carbon atoms.

5. The method as defined in claim 1 wherein the surfactant specified is the potassium salt of a mixture of perfluoro-alkanoic acids of from about eight to about 10 carbon atoms.

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