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3,003,877

SPOT PREVENTION IN PHOTOGRAPHIC EMULSIONS AND COLLOID LAYERS

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No Drawing. Filed June 27, 1957, Ser. No. 668,316
16 Claims. (Cl. 96—94)

This invention relates to improved photographic coatings comprising a synthetic spreading agent and tannic acid.

It is known that saponin can be used in gelatin coating compositions for the purpose of obtaining uniform coatings substantially free of bare spots and other surface imperfections. It is also known that commercial saponin varies considerably from batch to batch, such variations making it quite difficult at times to obtain uniform results in the coatings.

It has been previously proposed to replace commercial saponin or soap bark extract with certain synthetic coating aids which can be manufactured to give uniform results in the coatings. For example, Knox et al. U.S. Patent 2,739,891, issued March 27, 1956, describes a class of aminosulfonic acid salts which can be used to replace the conventional saponin coating aid. Other synthetic coating aids are described in Knox et al. U.S. application Serial No. 556,044, filed December 29, 1955; Knox et al. U.S. application Serial No. 600,679, filed July 30, 1956, and Wilson et al. U.S. application Serial No. 603,195, filed August 9, 1956.

While such synthetic coating agents have provided material benefits not obtainable with commercial saponin, they generally lack certain of the desirable properties contributed by the tannic acid of the extract. Certain photographic coating solutions contain minute metallic iron or iron compounds as impurities and when photographic coatings containing such impurities and the synthetic coating aids are processed in the normal manner, small desensitized areas, or areas of reduced density appear in the course of the process. These small areas of reduced density show up as white spots, thus producing a rather serious defect in the final photographic print.

An effort has been made to overcome the undesirable effect produced by the metallic iron or iron compounds by using various chelating agents, such as derivatives of ethylenediamine tetracetic acid and the like. However, these chelating agents have not been effective in eliminating the small areas of reduced density or white spots.

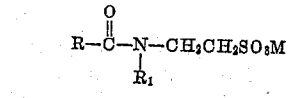
We have found that the aforementioned benefits of the synthetic spreading agents can be retained, while eliminating their serious side effects by adding small amounts of tannic acid to the coating solution. By tannic acid we mean m-digallic acid (approx. $C_{14}H_{10}O_9$, M.W=322.23).

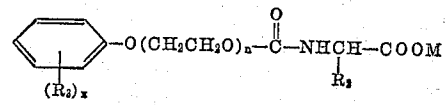
It is, therefore, an object of our invention to provide an improved means of obtaining uniform gelatin coatings for photographic use. Another object is to provide a means of avoiding reduced density areas when synthetic spreading agents are used in preparing photographic gelatin coatings. Other objects will become apparent from a consideration of the following examples and description.

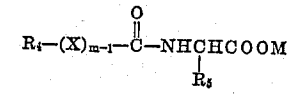
We have found that tannic acid can be added directly to ordinary gelatino-silver-halide emulsions containing synthetic spreading agents as coating aids, or to other photographic gelatin coating solutions containing no light-sensitive material, such as the coatings generally employed in imbibition printing blanks. Alternatively, the tannic acid can be added to gelatin coating solutions

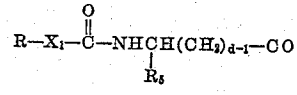
which are placed in contact with conventional gelatino-silver-halide layers. Of course, when placing the tannic acid in a layer contiguous to the light-sensitive layer, it is generally desirable to use a larger quantity of tannic acid in the coating solution.

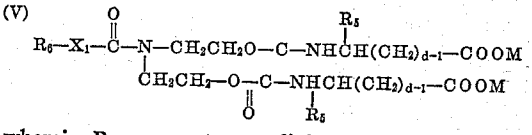
The synthetic coating aids used as a replacement for commercial saponin are generally compounds containing a hydrophobic moiety, such as a long-chain alkyl group, in combination with a hydrophilic moiety, such as sulfonic acid salt groups or carboxylic acid salt groups. These synthetic coating aids frequently have an amido group somewhere in the chain. These synthetic coating aids can be classified generically as water-soluble salts of sulfonic or carboxylic acids containing an amido group. While representative synthetic coating aids or spreading agents are illustrated below, it is to be understood that other synthetic agents can be employed to equal advantage in accomplishing the beneficial results afforded by the tannic acid of our invention. Typical coating aids include those represented by the following general formulas:

(I)


(II)


(III)


(IV)


(V)


wherein R represents an aliphatic hydrocarbon radical containing at least 8 carbon atoms (e.g., n-octyl, n-decyl, n-myristyl, n-cetyl, oleyl, linoleyl, etc.), R_1 represents an aliphatic radical containing not more than about 4 carbon atoms (e.g., methyl, ethyl, n-propyl, n-butyl, etc.), a cycloalkyl group (e.g., cyclopentyl, cyclohexyl, etc.), or an aryl group (e.g., phenyl, tolyl, etc.), R_2 represents a hydrogen atom, a lower alkyl group (e.g., methyl, ethyl, etc.), a water-soluble carboxylic acid group or a water-soluble carboxyalkyl group (e.g., carboxymethyl, carboxyethyl, etc.), R_3 represents a hydrogen atom or an alkyl group containing at least 5 carbon atoms (e.g., n-amyl, n-octyl, etc., such as alkyl groups containing from 5 to 18 carbon atoms, so that the total number of carbon atoms in the R_3 groups is at least 10), R_4 represents the carbocyclic nucleus of a rosin acid, such as rosinyl, hyrorosinyl, dihydrorosinyl, etc., radicals, R_5 represents a lower alkyl group (e.g., methyl, ethyl, etc.), an aryl group (e.g., phenyl, tolyl, etc.), a water-soluble carboxylic acid salt group or a water-soluble salt of a carboxyalkyl group (e.g., carboxymethyl, carboxyethyl, etc.), R_6 represents an aliphatic hydrocarbon radical containing at least 8 carbon atoms (such as those radicals listed above with respect to R) or an alkaryl group, the alkyl portion of which contains at least 8 carbon atoms (e.g.,

n-octyl, n-decyl, etc.), M represents an alkali metal atom (e.g., sodium, potassium, etc.), ammonium or organic ammonium (i.e., derivatives where a salt has been formed between the sulfonic acid and an organic amine, such as pyridine, triethylamine, triethanolamine, etc.), *n* represents a positive integer from 1 to 12, *x* represents a positive integer of from 1 to 4, *m* represents a positive integer of from 1 to 2, *d* represents a positive integer of from 1 to 3, X represents a methylene oxy group ($—CH_2O—$), a methylene amino group ($—CH_2NH—$) or the group $—CH_2O(CH_2CH_2O)_n$ where *n* has the values given above, and X_1 represents a divalent oxygen atom, the group $—CONHCH_2CH_2O—$ or $—O(CH_2CH_2O)_n—$ where *n* has the values given above.

The synthetic spreading agents represented by Formula I above can be prepared as described in U.S. Patent 2,739,891. Among the useful synthetic spreading agents disclosed in the patent are the alkali metal salts of oleoyl methyl taurine.

The synthetic spreading agents represented by Formula II above can be prepared according to the method described in application Serial No. 556,044 mentioned above, as well as U.S. application Serial No. 600,679. Useful synthetic spreading agents shown in these applications include N-(carbo-p-tertiary octyl phenoxy pentaethoxy) glutamate disodium salt, N-carbo-β-oleamido ethoxy aspartic acid sodium salt, etc.

The synthetic spreading agents represented by Formula III above can be prepared as described in Serial No. 603,195 mentioned above. Typical of such synthetic spreading agents are sodium N-carbo-abityl oxy glutamate, N-carbo-abityl-oxy polyethoxy glycine sodium salt, etc.

The synthetic spreading agents represented by Formulas IV and V above can be prepared as described in Serial No. 600,679 mentioned above. Typical spreading agents include 3,8,13-triaza-4,12-dioxo-5,11-dioxa-8-lauroyl pentadecane-1,15-dioic acid sodium salt, etc.

Other synthetic spreading agents useful in our invention include the alkali metal salts of maleopimaric acid, which is disclosed in U.S. Patent 2,628,226. The use of this particular type of synthetic spreading agent is disclosed in Serial No. 556,044 mentioned above.

Other synthetic spreading agents, which can be used in place of saponin to provide the useful results illustrated below, are tetrasodium maleopimaroyl glutamate, tetrasodium maleopimaroyl aspartate and similar maleopimaroyl derivatives of amino aliphatic polycarboxylic acids.

The amounts of synthetic spreading agents useful in our invention are well known to those skilled in the art. The useful amounts of these agents have been previously described in the references referred to above. For example, oleoyl methyl taurine can be used in an amount varying from about .0055 to .5%, based on the amount of dry gelatin in the coating composition. The most useful amount for a given spreading agent can be determined by running a series of test coatings, wherein the amounts of spreading agent are varied. The point at which the uniform spreading occurs without the formation of dry areas in the coating can be readily observed.

In like manner, the amount of tannic acid used in our invention can be varied, depending upon the source of the gelatin, particular spreading agent being used, and the like. In general, we have found that from about .065 gram to .65 gram per 100 square feet of coated area is sufficient for the purposes of our invention.

When used in gelatino-silver-halide emulsions, it has been noted that particularly useful results have been obtained with the so-called paper emulsions containing silver chlorobromide. However, other gelatino-silver-halide emulsions, such as silver chloride, silver bromiodide, silver chlorobromiodide, etc. emulsions can also be treated according to our invention.

The following examples will serve to illustrate more fully the manner of practicing our invention.

Example 1

An ordinary gelatino-silver-chlorobromide emulsion was divided into several batches, and these batches treated with the amounts of tannic acid shown in the following table. Certain of the batches contained sufficient spreading agent to insure uniform coating, these spreading agents being identified in the table. The various emulsions were then coated on an ordinary photographic paper support and the coatings dried and processed in the usual manner. The number of white spots per 8" by 10" sheet were measured for the fresh coatings, as well as for the coatings after incubation for eight days at 120° F. and three months under storage under ambient conditions. The number of white spots for each of the three conditions is given in the following table.

g./100 sq. ft. Tannic Acid	Spreading Agent	White Spots, Fresh	White Spots, 8 day Incubation	White Spots, 3 Months
0	soap bark [1]	2	7	21
.098	do.[1]	1¾	2	3
.325	do.[1]	<1	0	1
.65	do.[1]	1	<1	0
0	SMP	4	35	78
.098	SMP	1¾	2	6
.195	SMP		2	3
.325	SMP	2	1	1
.65	SMP	1	<1	1

[1] Extract.

Example 2

The same emulsion batch used in Example 1 above was divided into two portions. To one of these portions was added a 3% solution of soap bark extract, sufficient solution being added to provide 60 cc. per 100 square feet of coating. The other portion was coated without treatment. The two coatings were then dried and processed in the usual manner. The number of white spots per 8" by 10" sheet was measured for fresh coatings, coatings which had been aged for six weeks at room temperature and coatings which had been aged for three months at room temperature. The following results were obtained.

Soap Bark Extract	White Spots, Fresh	White Spots, 6 Weeks	White Spots, 3 Months
60 cc./100 sq. ft.	5	7	5
0	26	33	35

This example shows that some ingredient present in soap bark extract has the property of preventing white spots in photographic paper emulsions during processing. Of course, the coatings of this example suffered from the ordinary defects accompanying the use of commercial saponin.

Example 3

The same emulsion used in Example 1 was treated with the spreading agents indicated below and the white spots per 8" by 10" sheet measured for each of the processed coatings. The results were as follows.

Spreading Agent	White Spots, Fresh	White Spots, 8 Day Incubation (120° F.)
SMP	21	157
Soap bark extract (clarified)	3	65
Commercial saponin	1	51

Tannic acid can be added to coatings containing clarified soap bark extract to improve the properties of such coatings, insofar as the prevention of white spots during processing is concerned. The following tabulation will

show this effect, the number of white spots given in the table being based on an 8" by 10" sheet.

g./100 sq. ft. Tannic Acid	White Spots, Fresh	White Spots, 8 Day Incubation (120° F.)	White Spots, 3 Months' Natural Aging
0	1⅛	16	35
.260	<1	1⅜	3

The abbreviation SMP used in the above examples means the sodium salt of maleopimaric acid.

Example 4

In the manner illustrated in Example 1, an ordinary gelatino-silver-chlorobromide emulsion was divided into several batches, and each of these batches treated with a spreading agent as identified in the table, alone and in combination with tannic acid. The emulsions were then coated on a paper support and processed as described above. The number of white spots per 8" by 10" sheet were measured for the fresh coatings, as well as for the coatings after incubation for eight days at 120° F. and three months storage under room conditions. The number of white spots for each of the coatings is given in the following table.

Spreading Agent	Tannic Acid, g./100 sq. ft.	White Spots, Fresh	White Spots, 8 day incubation	White Spots, 3 months
none	0	5	37	111
Do	.13	1	3	18
Soap bark extract	0	<1	3	41
Do	.13	<1	1	5
OMT	0	6	12	26
OMT	.13	2	3	2
OPEG	0	<1	11	80
OPEG	.13	0	2	3
MPG	0	<1	19	112
MPG	.13	<1	2	16

In the above table, OMT means oleoyl methyl taurine, OPEG means N-(carbo-p-tertiary octyl phenoxy pentaethoxy) glutamate disodium salt and MPG means tetrasodium maleopimaroyl glutamate.

In the above incubation tests, it is to be understood that the coatings were aged under these conditions prior to exposure and processing. The exposures in the above example were sufficient to produce a uniform medium density and conventional development, such as by Kodak's D–52 developer, was employed. Kodak's D–52 developer has the following composition:

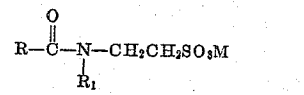
	G.
N-methyl-p-aminophenol sulfate	1.5
Sodium sulfite, anhydrous	22.5
Hydroquinone	6.3
Sodium carbonate, anhydrous	15.0
Potassium bromide	1.5

Water to make 1 liter.

While our invention has been described with reference particularly to gelatino-silver-halide emulsions intended for black-and-white photography, it is to be understood that our invention can also be applied to gelatin compositions intended for use in color photography. Thus, tannic acid can be used in combination with conventional synthetic spreading agents of the type described above, these ingredients being incorporated in a gelatino-silver-halide emulsion containing color-forming compounds or couplers. Such couplers are generally non-diffusing in the photographic treating solutions customarily employed in color photography. Such color couplers include the oil-soluble couplers, such as 1-phenyl-{3-[2-(2,4-diamylphenoxy)-5(2-sulfobenzamido)benzamido}-5-pyrazolone. Such emulsions can contain conventional gelatin hardening agents, such as mucochloric acid, although it has been found that bis-esters of methane sulfonic acid of the type described in Allen et al. U.S. Patent 2,726,162 are particularly useful since they reduce stain. Typical of such hardening agents are 1,5-di(methane sulfonoxy)-pentane 1,2-di(methane sulfonoxy)ethane, etc.

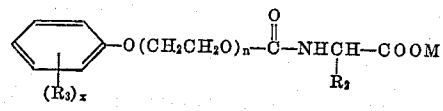
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A gelatin coating composition comprising (1) gelatin, (2) a synthetic spreading agent selected from those represented by the following general formula:



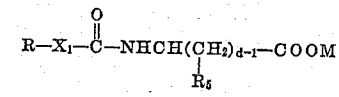
wherein R represents an aliphatic hydrocarbon radical containing at least eight carbon atoms, R_1 represents a member selected from the group consisting of an aliphatic radical containing one to four carbon atoms, a cycloalkyl group and an aryl group, and M represents a member selected from the group consisting of an alkali metal atom, an ammonium group and an organic ammonium group, and (3) tannic acid.

2. A gelatin coating composition comprising (1) gelatin, (2) a synthetic spreading agent selected from those represented by the following general formula:



wherein R_2 represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group, a water-soluble carboxylic acid group and a water-soluble carboxyl alkyl group, R_3 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 5 to 18 carbon atoms, M represents a water-soluble cation, *n* represents a positive integer of from 1 to 12, and *x* represents a positive integer of from 1 to 4, and (3) tannic acid.

3. A gelatin coating composition comprising (1) gelatin, (2) a synthetic spreading agent selected from those represented by the following general formula:

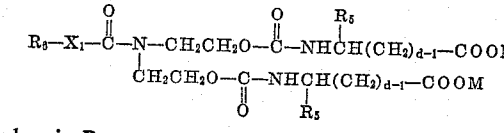


wherein R represents an aliphatic hydrocarbon radical containing at least 8 carbon atoms, R_5 represents a member selected from the group consisting of a lower alkyl group, a water-soluble carboxylic acid salt group and a water-soluble carboxy alkyl group, M represents a water-soluble cation, X_1 represents a member selected from the group consisting of a divalent oxygen atom, a

$$—CONHCH_2CH_2O—$$

group and a $—O(CH_2CH_2O)_n—$ group, *n* represents a positive integer of from 1 to 12, and *d* represents a positive integer of from 1 to 3, and (3) tannic acid.

4. A gelatin coating composition comprising (1) gelatin, (2) a synthetic spreading agent selected from those represented by the following general formula:



wherein R_5 represents a member selected from the group consisting of a lower alkyl group, a water-soluble carboxylic acid salt group, and a water-soluble carboxy alkyl group, R_6 represents a member selected from the group consisting of an aliphatic hydrocarbon radical containing at least 8 carbon atoms and an aryl group, the alkyl portion of which contains at least 8 carbon atoms, X_1 represents the member selected from the group consisting of a divalent oxygen atom, a $—CONHCH_2CH_2O—$

group and a $-O(CH_2CH_2O)_n-$ group, n represents a positive integer of from 1 to 12, M represents a water-soluble cation and d represents a positive integer of from 1 to 3, and (3) tannic acid.

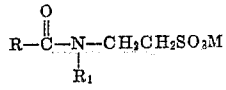
5. A gelatin coating composition comprising (1) gelatin, (2) oleoyl methyl taurine, and (3) tannic acid.

6. A gelatin coating composition comprising (1) gelatin, (2) sodium maleopimarate, and (3) tannic acid.

7. A gelatin coating composition comprising (1) gelatin, (2) N-(carbo-p-tertiary octyl phenoxy pentaethoxy) glutamate disodium salt, and (3) tannic acid.

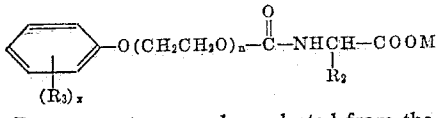
8. A gelatin coating composition comprising (1) gelatin, (2) tetrasodium maleopimaroyl glutamate, and (3) tannic acid.

9. A photographic gelatino-silver-halide emulsion comprising (1) a synthetic spreading agent selected from those represented by the following general formula:



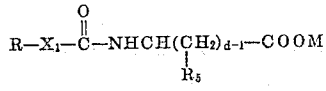
wherein R represents an aliphatic hydrocarbon radical containing at least eight carbon atoms, R_1 represents a member selected from the group consisting of an aliphatic radical containing one to four carbon atoms, a cycloalkyl group and an aryl group and M represents a member selected from the group consisting of an alkali metal atom, an ammonium group and an organic ammonium group, and (2) tannic acid.

10. A photographic gelatino-silver-halide emulsion comprising (1) a synthetic spreading agent selected from those represented by the following general formula:



wherein R_2 represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group, a water-soluble carboxylic acid group and a water-soluble carboxy alkyl group, R_3 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 5 to 18 carbon atoms, M represents a water-soluble cation, n represents a positive integer of from 1 to 12, and x represents a positive integer of from 1 to 4, and (2) tannic acid.

11. A photographic gelatino-silver-halide emulsion comprising (1) a synthetic spreading agent selected from those represented by the following general formula:

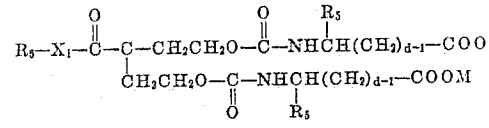


wherein R represents an aliphatic hydrocarbon radical containing at least 8 carbon atoms, R_5 represents a member selected from the group consisting of a lower alkyl group, a water-soluble carboxylic acid salt group and a water-soluble carboxy alkyl group, M represents a water-soluble cation, X_1 represents a member selected from the group consisting of a divalent oxygen atom, a

$$-CONHCH_2CH_2O-$$

group and a $-O(CH_2CH_2O)_n-$ group, n represents a positive integer of from 1 to 12, and d represents a positive integer of from 1 to 3, and (2) tannic acid.

12. A photographic gelatino-silver-halide emulsion comprising (1) a synthetic spreading agent selected from those represented by the following general formula:



wherein R_5 represents a member selected from the group consisting of a lower alkyl group, a water-soluble carboxylic acid salt group, and a water-soluble carboxy alkyl group, R_6 represents a member selected from the group consisting of an aliphatic hydrocarbon radical containing at least 8 carbon atoms and an alkaryl group, the alkyl portion of which contains at least 8 carbon atoms, X_1 represents the member selected from the group consisting of a divalent oxygen atom, a

$$-CONHCH_2CH_2O-$$

group and a $-O(CH_2CH_2O)_n-$ group, n represents a positive integer of from 1 to 12, M represents a water-soluble cation and d represents a positive integer of from 1 to 3, and (2) tannic acid.

13. A photographic gelatino-silver-halide emulsion containing sodium maleopimarate and tannic acid.

14. A photographic gelatino-silver-halide emulsion containing N-(carbo-p-tertiaryoctyl phenoxy pentaethoxy) glutamate disodium salt and tannic acid.

15. A photographic gelatino-silver-halide emulsion containing oleoyl methyl taurine and tannic acid.

16. A photographic gelatino-silver-halide emulsion containing tetrasodium maleopimaroyl glutamate and tannic acid.

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UNITED STATES PATENT OFFICE

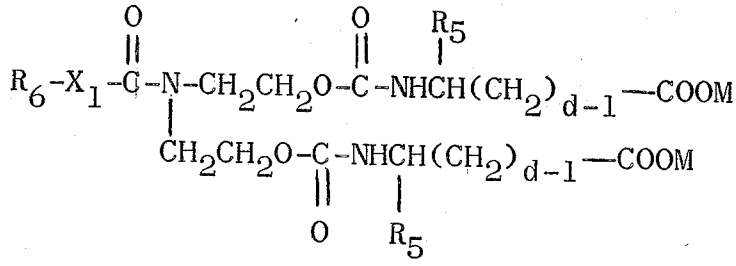
CERTIFICATION OF CORRECTION

Patent No. 3,003,877 October 10, 1961

Leonard T. McLaughlin et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 72, for "aryl" read -- alkaryl --; column 8, lines 14 to 19, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 17th day of April 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents