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3,561,967

**PHOTOGRAPHIC LIGHT-SENSITIVE
SILVER HALIDE ELEMENTS**

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41/57,486

Int. Cl. G03c 1/04

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9 Claims

ABSTRACT OF THE DISCLOSURE

By incorporating a water-soluble high-molecular compound having at least one aromatic sulfonic acid group in a gelatino silver-halide emulsion layer of a photographic light-sensitive film which contains a nonionic water-soluble high-molecular compound, such as, hydroxyethyl cellulose or polyvinyl alcohol, the formation of haze is reduced and the miscibility of gelatin with the nonionic high-molecular compound is improved.

BACKGROUND OF THE INVENTION**(1) Field of the invention**

The present invention relates to a photographic light-sensitive element having an improved layer containing gelatin and nonionic water-soluble high molecular compound.

(2) Description of the prior art

As a protective colloid for a light-sensitive silver halide, gelatin has usually been used at present. This is because gelatin has excellent photographic and physical properties, but gelatin has several disadvantages. For instance, since gelatin is a natural material, the properties thereof are markedly influenced by the kind of raw materials to be employed and the method of the production thereof. Hence, it is difficult to obtain a product having a constant quality. Gelatins is expensive and tends to be attacked by microorganisms. Also, gelatin is unstable to changes of temperature and humidity.

Recently, it has been attempted to use various synthetic high molecular weight compounds as a protective colloids for light-sensitive silver halide in photographic emulsions to overcome such difficulties. However, such attempts are accompanied by other difficulties. For example, the preparation of high speed photographic emulsions is difficult, the removal of soluble halides formed at the formation of silver halide is difficult, since such high molecular weight compounds do not form reversible gels responsive to temperature change, and, also, the strength of the layer is weak, since it is difficult to obtain suitable hardening agents for synthetic high molecular weight compounds. Therefore, for preparing a photographic emulsion having both the excellent photographic properties of gelatin and the merits of synthetic high molecular weight compounds, it has been proposed to replace part of the gelatin with a synthetic high molecular weight compound. For example, by incorporating in a gelatino silver halide

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emulsion a suitable water-soluble high molecular weight compound, curing of the film can be prevented, the drying speed of the film can be shortened, and, also, the covering power of developed silver can be increased.

On the other hand, in the case of replacing a part of gelatin with a water-soluble high molecular weight compound, a non-ionic water-soluble high molecular weight compound is not easily mixed with gelatin in any desired mixing ratio to cause a so-called de-mixing phenomenon. That is, if the proportion of the non-ionic high molecular weight compound is high, although a warm aqueous solution of the non-ionic high molecular compound is once compatible with a warm aqueous solution of gelatin, on cooling, the non-ionic high molecular weight compound is separated from gelatin. Hence, the non-ionic water-soluble high molecular weight compound is present irregularly in the coagulated gelatin, and, also, the dried film does not have a homogeneous phase. Furthermore, since the water-soluble high molecular weight compound itself is aggregated, coated and processed, the emulsion layer deteriorates and shows a tendency toward turbidity and haziness. Moreover, since silver halide particles are dispersed in gelatin, the graininess of the developed silver increases. When the proportion of the non-ionic high molecular weight compound to gelatin is low, these phenomena will occur only slightly, but when the proportion of the former is higher than 20% by weight of gelatin, these phenomena will occur to a great extent.

Therefore, an object of this invention is to provide photographic elements which have coated photographic emulsions of improved quality. A further object is to provide such elements which have reduced haze and improved transparency, despite the use in the photographic emulsions of non-ionic high molecular compounds. A still further object is to provide such elements which result in diminished graininess of developed silver by improving the miscibility of gelatin with a non-ionic high molecular compound. Other objects will appear hereinafter.

SUMMARY OF THE INVENTION

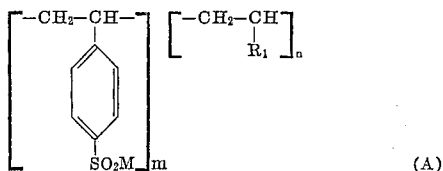
These and other objects have been accomplished by the following invention which comprises a method of using a synthetic water-soluble high molecular weight compound having an aromatic sulfonic acid group in a gelatin layer containing a non-ionic, water-soluble, high molecular weight compound.

As the non-ionic water-soluble high molecular weight compound used in the present invention, there are illustrated polymers of acrylamide and derivatives thereof, such as, N-methylacrylamide, N-ethylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-methoxymethylacrylamide, N-ethoxymethylacrylamide, N-morpholinoacrylamide, N-morpholinomethylacrylamide and the like; vinyl polymers such as polyvinyl alcohol, polyvinyl methyl ether, polyvinyl pyrrolidone, polyvinylloxazolidone, polyvinyl caprolactam and the like; soluble starches, such as, dextrin, alkylated starch and the like; and cellulose derivatives such as hydroxyethyl cellulose, methyl cellulose and the like. Furthermore, water-soluble copolymer of them may be used.

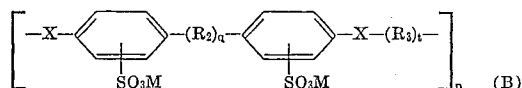
In the present invention various water-soluble high molecular weight compounds having aromatic sulfonic acid groups may be used. Illustrated use of such com-

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pounds are the high molecular weight compounds represented by the following general formulae:



wherein R_1 is a substituted amide group, an unsubstituted amide group, $-\text{OCOR}$; $-\text{COOR}'$ (R' and R'' are an alkyl group) a halogen, $-\text{OH}$, and $-\text{CN}$; M is an alkali metal; m is a positive integer; and n is 0 or a positive integer; and

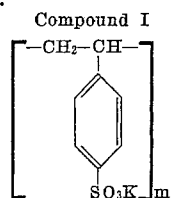


wherein X is $-\text{OCO}_2-$, $-\text{OCO}-$, $-\text{NHCO}-$, $-\text{NHCONH}-$

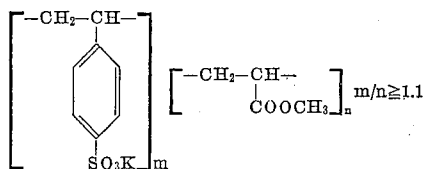
$-\text{NHSO}_2$, and $-\text{OSO}_2-$; R_2 is a divalent saturated or unsaturated aliphatic group; q is 0 or 1; R_3 is a divalent aliphatic group or a divalent aromatic group, t is 0 or 1; and p is a positive integer.

It is preferable to use water-soluble high molecular weight compounds having at least one aromatic sulfonic acid group per molecular weight of 300 in the present invention. For example, in the case of using as the non-ionic water-soluble high molecular weight compound a polyvinyl alcohol which has very low miscibility with gelatin, if the number of aromatic sulfonic acid groups per molecular weight of 300 is less than 1, it is necessary to add a great amount thereof to obtain a homogeneous system, while the use of a compound having more than one aromatic sulfonic acid group per molecular weight of 300 is very effective.

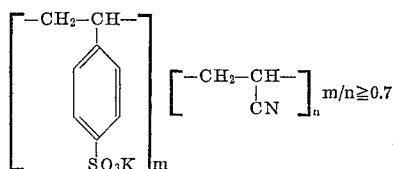
The practical examples of the water-soluble high molecular weight compounds having aromatic sulfonic acid groups used in the present invention are shown below, in which m/n is a value such that the number of aromatic sulfonic acid groups per molecular weight of 300 is more than 1:



Compound II

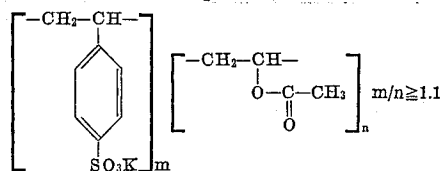


Compound III

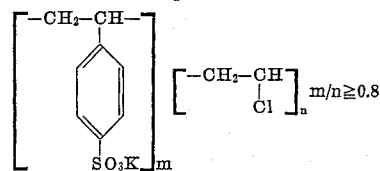


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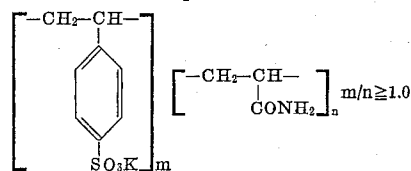
Compound IV



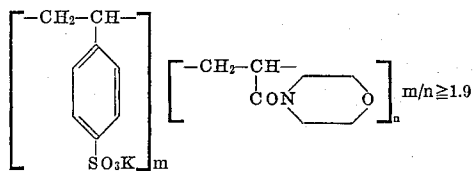
Compound V



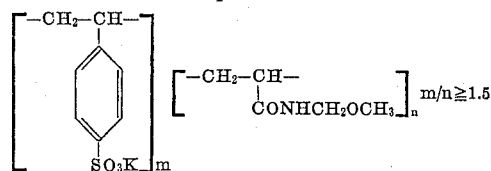
Compound VI



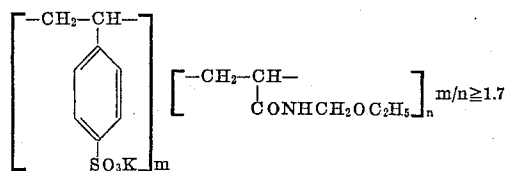
Compound VII



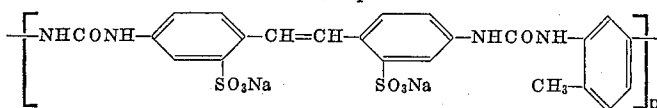
Compound VIII



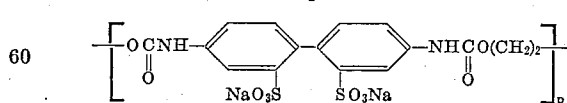
Compound IX



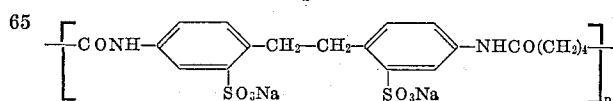
Compound X



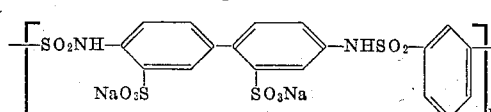
Compound XI

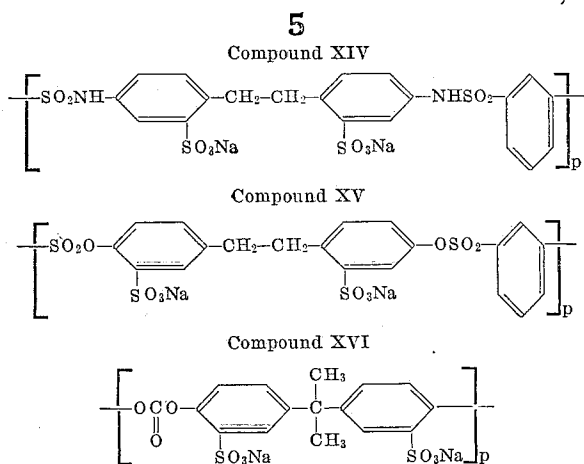


Compound XII



Compound XIII





Compounds I-IX may be prepared by polymerizing an alkali metal salt of p-styrenesulfonic acid alone, or copolymerizing it with a corresponding copolymer, as described in Japanese Pat. No. 3,582/60. The arrangement of the copolymers in the molecule of the copolymer has not yet been clearly determined.

Moreover, methods for preparing Compounds X-XII are disclosed in British Pat. No. 867,539 and methods for preparing Compounds XIII-XVI are disclosed in, for example, Japanese Pats. 22,472/65, 22,470/65, and 22,471/65.

The non-ionic water-soluble high molecular compounds (group A) and the water-soluble high molecular compounds having aromatic sulfonic acid groups (group B) used in the present invention may be incorporated in an emulsion in any step in the preparation of the emulsion. For example, a gelatino silver halide emulsion may be prepared in the presence of a compound belonging to group B and, after water-washing, and post ripening, a compound belonging to group B may be added thereto. Or, a compound belonging to group A may be added to a gelatino silver halide emulsion directly before coating and a compound belonging to group B may be added thereto. Furthermore, an aqueous solution containing a compound belonging to group A and a compound belonging to group B may be added to a gelatino silver halide emulsion. By employing any method as mentioned above, a uniformly coated layer can be obtained.

The high molecular weight compound may be added as a solid to the gelatino silver halide emulsion to be dissolved therein but it is convenient to add it as an aqueous solution thereof having a proper concentration.

The addition amount of the water-soluble high molecular weight compound having aromatic sulfonic acid groups is influenced by the kind and amount of gelatin and the non-ionic water-soluble high molecular compound but the addition amount is generally more than 5% by weight, preferably, 10-100% by weight based on the weight of the non-ionic water-soluble high molecular compound. In the case of employing the non-ionic, water-soluble compound which is particularly immiscible with gelatin, such as, polyvinyl alcohol and hydroxyethyl cellulose, a good result can be obtained by adding more than 25% by weight of it. The addition of the water-soluble compound having aromatic sulfonic acid groups can be in an amount of more than 100% by weight, but since the effect of the addition thereof does not correspond to the increase in the addition amount, the addition of such a higher amount is unnecessary, as well as undesirable, because it may be accompanied by faults, such as, viscosity increase.

The present invention may be applied to any type of silver halide emulsions, such as, a silver chloride emulsion, a silver bromide emulsion, a silver bromochloride emulsion, a silver iodobromide emulsion and a silver chloriodo-bromide emulsion.

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The silver halide emulsion to which the present invention is applied may be chemically sensitized in a known manner, such as, by adding a compound containing unstable sulfur, such as, ammonium thiosulfate or allylthio urea (P. Glafkides: "Chimie Photographique," 2nd edition, 297-299 (1957), Photocinema, Paul Montel Paris) or by a gold compound (ibid., page 301), such as, a complex salt of mono-valent gold and thiocyanic acid, or by a combination thereof. Moreover, the emulsion may be optically sensitized by adding a dye sensitizer, such as, a cyanine dye or a merocyanine dye. Further, the emulsion may be stabilized by a heterocyclic compound, such as, benzothiazole, 1-phenyl-5-mercaptotetrazole, 4-hydroxy-6-methyl-1,3,3a,7-tetrazinedene, or 6-thioctic acid; a mercury compound such as mercuric acid (Japanese Pat. 22,063/64); benzenesulfonic acid and the like. Still further, the emulsion may be hardened by a hardening agent, such as, formaldehyde, mucochloric acid, chromium alum, or a triazine derivative (Belgian Pat. 641,044), or by using such a hardening agent together with a hardening aid, such as, resorcinol or resorcyaldehyde. The emulsion may further contain a surface active agent, such as, saponin, sodium alkylbenzene sulfonate, or an addition polymer of an alkylphenol and a sulfone (British Pat. 1,024,808) to facilitate coating. Furthermore, the emulsion may be sensitized by a polyalkyleneoxide derivative, such as, a condensation product of an alkylphenol and polyethyleneoxide.

The silver halide emulsion of the present invention may be used for the preparation of photographic color films and photographic color printing papers by incorporating therein a coupler. Further, since the coating layer of the emulsion of this invention can be removed by water washing after development by increasing the ratio of the water-soluble high molecular weight compounds to gelatin, the emulsion can be used as a negative layer in a so-called multi-layer diffusion system (Neblette; "Photography, Its Materials and Processes," 6th edition, 371-373 (1962); D. Van Nostrand Co., Princeton, N.J.). In the case of using the non-ionic high molecular weight compound having poor miscibility with gelatin, such as, polyvinyl alcohol or hydroxyethylcellulose, in such a use of the embodiment, it is desirable to use the non-ionic high molecular weight compound in an amount of more than 2, and particularly, about 5 times the weight of gelatin. Also, very excellent results can be obtained by using the water-soluble high molecular compound having aromatic sulfonic acid groups in an amount of more than 10% by weight, and particularly 25% by weight of the non-ionic high molecular compound.

The invention has been described in detail, above, only in the case of applying it to a silver halide emulsion layer, but it should be understood that the present invention can similarly be applied to other photographic layers such as a backing layer, a protective layer and intermediate layers.

According to the present invention, a desired amount of the non-ionic water-soluble high molecular compound may be added to gelatin, whereby curling dimensional stability, drying speed and covering power of the gelatin layer can be improved without reducing the quality, transparency and adhesiveness of the layer, and at the same time reducing the graininess of developed silver particles.

EXAMPLE 1

After adding the usual additives such as a dye, a hardening agent, a wetting agent and the like to 750 g. of a silver chlorobromide emulsion containing 41 g. of gelatin, the emulsion was divided into three parts, A, B, and C, and they were each mixed with the following compound:

- Part A: no additive
- Part B: mixed with 75 ml. of a 5% aqueous solution of hydroxyethylcellulose
- Part C: mixed with 75 ml. of a 5% aqueous solution of hydroxyethylcellulose and 12 ml. of a 5% aqueous solution of compound X

The hydroxyethylcellulose used in the example had a viscosity of 900 cp. of the 5% aqueous solution thereof at 25° C. and also the intrinsic viscosity of the 5% aqueous solution of compound X at 30° C. was 0.98. Each of emulsions A, B, and C was mixed uniformly and applied to an under-coated film base in a thickness of 10 microns. After drying, the light sensitive film was developed for 5 minutes at 20° C. in a developer having the following composition:

Warm water—500 ml.
Metol—2.5 g.
Sodium sulfite (anhydrous)—30.0 g.
Hydroquinone—2.5 g.
Borax—10.0 g.
Potassium bromide—0.5 g.
Water to make 1000 ml.

Thereafter, the film was subjected to conventional stopping, fixing, water-washing and drying procedures.

The light transmittance and the haze value of the fogged portion of the film were measured. The results are as follows:

	Transmittance, percent	Haze value
Film sample:		
A (control)-----	100	4.6
B (control)-----	55.5	47.1
C-----	77.8	20.1

The haze value was obtained by introducing the values of T_t (total transmittance) and T_d (diffusion transmittance) to the formula $T_d/T_t \times 100$ and the smaller the value, the lower the turbidity.

After mixing uniformly, each of the emulsions was mixed with usual additives, such as, dye, a hardening agent, a wetting agent and the like and then applied to an under-coated film base in a thickness of 10 microns. The film thus obtained was processed as in Example 1 and the transmittance and haze value of the unexposed portions were measured, the results of which are as follows:

	Transmittance, percent	Haze value
Film sample:		
A (control)-----	100	4.5
B (control)-----	84.7	30.5
C-----	90.5	12.1
D-----	96.2	10.0

From the results, it was clear that the transmittance and the haze of the emulsion layer containing a mixture of gelatin and polyvinyl alcohol was improved by the addition of compound I. Also, the films coated with emulsions C and D respectively had similar photographic properties and less curling tendency than those of the film coated with emulsion A.

EXAMPLE 3

The high molecular compounds shown in the following table were added to 250 g. of the same silver iodobromide emulsion as in Example 2 and the resulting emulsion was processed as in Example 1. Thereafter, the transmittance and the haze value of the unexposed portion of the film thus prepared were measured, the results of which are shown in the following table.

	Nonionic high molecular weight compound	High molecular weight compound having aromatic sulfonic acid groups	Transmittance	Haze value
A-----	None	None	100	4.5
B-----	Polyacrylamide 10%, 50 ml.	do	80.5	39.3
C-----	do	Compound VI 10%, 40 ml.	92.1	15.6
D-----	do	Compound VII 10%, 40 ml.	88.2	23.3
E-----	do	Compound XII 10%, 40 ml.	90.0	15.9
F-----	do	Compound XIII 10%, 40 ml.	89.3	16.8
G-----	do	Compound XVI 10%, 40 ml.	88.7	17.0

As is clear from the above results, the transparency after processing of the film coated with the emulsion having incorporated therein compound X and hydroxyethylcellulose was higher and haze thereof was lower than those of the film coated with the emulsion having incorporated therein hydroxyethylcellulose alone. Further, the film coated with emulsion C had the same photographic properties, and less curling tendency than those of the film coated with emulsion A.

EXAMPLE 2

One kilogram (1 kg.) of a silver iodobromide emulsion containing 5% gelatin was divided into 4 equal portions and each of them was added with the following compounds:

Part A: no additive

Part B:

Polyvinyl alcohol—5 g.
Water—50 ml.

Part C:

Polyvinyl alcohol—5 g.
Compound I—0.5 g.
Water—50 ml.

Part D:

Polyvinyl alcohol—5 g.
Compound I—1 g.
Water—50 ml.

The polyvinyl alcohol used in the example was GL-05 (trade name of Nippon Gosei Kagaku K. K.) having a saponification value of 88% and molecular weight of 500, and the intrinsic viscosity of an aqueous solution of compound I at 30° C. was 11.0.

The high molecular weight compounds used herein were as follows:

	Intrinsic Viscosity ¹
Polyacrylamide-----	3.5
Compound VI-----	1.3 ($m/n=1.6$)
Compound VII-----	0.45 ($m/n=3.7$)
Compound XII-----	0.09
Compound XIII-----	0.11
Compound XVI-----	0.16

¹ At 30° C. (solvent: water)

From these results, it will be understood that the transmittance and the haze of the film coated with the silver halide emulsion containing gelatin and polyacrylamide can be improved by the addition of any compounds VI, VII, XII, XIII and XVI. Also by using these compounds, photographic light-sensitive films having improved photographic properties can be obtained, without lowering the sensitizing effect of polyacrylamide.

EXAMPLE 4

After adding a color toning agent, a hardening agent and a wetting agent to one kg. of a 6.5% aqueous gelatin solution containing 0.2 g. of colloidal silver sulfide nuclei and 10 g. of borax, the gelatin solution was coated on an under-coated film base in a thickness of 3.0 microns. To the gelatin layer thus formed there was applied a gelatin silver chlorobromide emulsion containing 2% gelatin and a mixed solution of 450 ml. of a 10% aqueous solution of polyvinyl alcohol, GL-05 (made by Nippon Gosei Kagaku K. K.) and 250 ml. of a 5% aqueous solution of compound I (intrinsic viscosity 11 at 30° C.) per 65 g. of said emulsion together with a stabilizer and a

wetting agent in a thickness of 8 microns to provide photographic layers for a so-called multilayer diffusion transfer system. In this case, when the polyvinyl alcohol alone was added to the silver chlorobromide emulsion without adding compound I, the mixed solution of gelatin and polyvinyl alcohol caused de-mixing to precipitate the silver chlorobromide emulsion. However, when compound I was added to the system, the system formed uniform solution. By applying it to a film base and drying, a good emulsion layer, in which the silver chlorobromide particles were uniformly dispersed, was obtained. The photographic film thus formed was exposed and developed for 3 minutes at 20° C. in a developer having the following composition:

Warm water—500 ml.

Metol—1.5 g.

Sodium sulfite (anhydrous)—22.5 g.

Hydroquinone—6.0 g.

Sodium carbonate (anhydrous)—40.0 g.

Sodium thiosulfate (anhydrous)—5.0 g.

Potassium bromide—1.0 g.

Water to make 1000 ml.

After immersing the film developed in a stopping solution for 20 seconds, the film was placed in a water stream, whereby the upper layer was naturally removed to leave a transferred positive image on the lower layer. Since the content of the water-soluble high molecular compounds was very much larger than that of gelatin, the upper layer containing them could be easily stripped off in a water stream. Hence, it was unnecessary to use an intermediate layer as is usually employed in a conventional multi-layer diffusion transfer system.

What is claimed is:

1. A photographic element comprising a photographic silver halide layer superimposed on a support and, incorporated in at least one layer of said photographic element, gelatin, more than 20% by weight, based on gelatin of a non-ionic water-soluble high molecular weight compound, and a water-soluble polymeric high molecular weight compound having aromatic sulfonic acid groups,

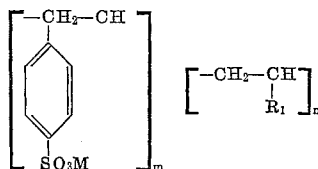
(a) said non-ionic water-soluble high molecular weight compound being selected from the group consisting of polyacrylamide a polymer of an acrylamide derivative, a polymethacrylamide, a polymer of a methacrylamide derivative, a vinyl polymer, a soluble starch, and a cellulose derivate,

(i) said acrylamide derivative being selected from the group consisting of alkylacrylamides, alkyl-etheracrylamides, and morpholinoacrylamides;

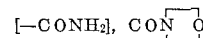
(ii) said methacrylamide derivative being selected from the group consisting of alkyl ethermethacrylamides and morpholinomethacrylamides;

(iii) said cellulose derivative being selected from the group consisting of hydroxyalkyl and alkyl cellulose derivatives;

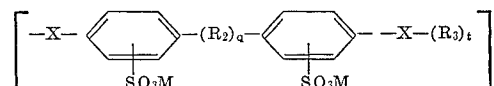
(b) said water-soluble polymeric high molecular weight compound having aromatic sulfonic acid groups being selected from the group consisting of compounds represented by the general formula:



wherein R₁ is a member selected from the group consisting of a substituted amide group selected from the group consisting of



CONHCH₂OCH₃ and CONHCH₂OC₂H₅, an unsubstituted amide group, —OCOR', —COOR'', where R' and R'' are alkyl groups, halogens, —OH and —CN; M is an alkali metal, m is a positive integer, and n is 0 or a positive integer, and



wherein X is a member selected from the group consisting of —OCO₂—, —OCO—, —NHCO—, —NHCOO—, —NHCONH—, —NHSO₂— and —OSO₂—; R₂ is a member selected from the group consisting of a di-valent saturated aliphatic group and a di-valent unsaturated aliphatic group, R₃ is a member selected from the group consisting of a di-valent aliphatic group and a di-valent aromatic group, q is 0 or 1, t is 0 or 1, and p is a positive integer.

2. The photographic light-sensitive element according to claim 1 wherein said layer in which said materials are incorporated is a silver halide emulsion layer.

3. The photographic light-sensitive element according to claim 1 wherein said layer in which said materials are incorporated is a backing layer.

4. The photographic light-sensitive element according to claim 1 wherein said layer in which said materials are incorporated is a protective layer.

5. The photographic light-sensitive element according to claim 1 wherein said layer in which said materials are incorporated is an intermediate layer.

6. A photographic light-sensitive element of claim 1 wherein said water-soluble polymeric high molecular weight compound having aromatic sulfonic acid groups has at least one aromatic sulfonic acid group per molecular weight of 300.

7. The photographic light-sensitive element of claim 6 wherein the amount of said compound having aromatic sulfonic acid groups is from about 10 to about 100% by weight based on the weight of said non-ionic water-soluble high molecular weight compound.

8. The photographic light-sensitive element of claim 1 wherein said vinyl polymer is polyvinyl alcohol.

9. The photographic light-sensitive element of claim 1 wherein said cellulose derivative is hydroxyethylcellulose.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96—114, 114.7