United States Patent Office 3,157,502 Patented Nov. 17, 1964

3,157,562

STABILIZED PHYSICAL DEVELOPERS CONTAINING IONOGENIC SURFACTANTS

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No Drawing. Filed Oct. 8, 1959, Ser. No. 845,698
Claims priority, application Netherlands Oct. 11, 1958
7 Claims. (Cl. 96—49)

This invention relates to developers used in the purely physical developments of photographic images and to processes employing such developers.

In the usual type of development employed in photography, the so-called chemical development, the metal in the visual photographic image is obtained by the reduction of metal ions of the water insoluble metal compound present in the latent image in the exposed light sensitive layer.

The developing solution employed in chemical development initially does not contain any dissolved compounds of the visual image metal. However, after the chemical developer is used for a while it may contain in solution ions ofthe visual image metal.

In the purely physical development the intensification or development of the latent image is carried out by treating the latent image with a developing solution which contains a water soluble reducible metal compound and a photographic reducing agent.

In physical developing practically all of the metal in the resultant visual image is formed by the selective reduction of metal ions or complex metals anions supplied by said water soluble metal compound.

The term "photographic reducing agent" is to be understood herein to mean a compound which, in the dissolved state, is capable of reducing the said metal ions or complex metal anions into free metal and the activity of which in the physical developer under the conditions otherwise prevailing therein is accelerated by the presence of a photographic latent image so as to obtain a sufficiently selective deposition of metal on this latent image.

The photographic reducers which may be used in physical development are frequently similar to those which are also used in chemical development.

They often satisfy the formula

$$a\text{—}\left(\begin{array}{c}|\\C\\|\end{array}=\begin{array}{c}|\\C\\|\end{array}\right)_n\text{—}b$$

wherein C represents a carbon atom, *a* and *b* each represent hydroxyl (OH) groups, amino groups or substituted amino groups (NH_2, NHR, NRR′ wherein R and R′ are alkyl or aryl radicals groups), *n* is zero or an integer.

It is possible to distinguish three large classes of photographic reducing agents which correspond to the above general formula.

(1) That of the hydroquinone type: *a* and *b* both are OH groups. This class includes, in addition to hydroquinone itself, inter alia: pyrocatechol, pyrogallol, gallic acid and ascorbic acid.

(2) That of the aminophenol type: *a* is an OH-group and *b* is an amino group which is substituted or not substituted. This class includes inter alia: o- and p-aminophenol, p-methylaminophenolsulphate ("metol"), p-hydroxyphenylglycine ("Kodurol").

(3) That of the phenylenediamine type: *a* is an amino group or a mono-substituted amino group, *b* is an amino group which is substituted or non-substituted. This class includes inter alia: o- and p-phenylenediamine and N,N-diethyl-p-phenylenediamine.

In addition, there are some further photographic reducing agents which do not satisfy the above-mentioned formula, such as 1-phenyl-3-pyrazolidone ("Phenidone") and several inorganic photographic reducing agents, such

as ferrous, titanous and vanadous ions, which are commonly used in the form of complex compounds, for example the ferrous-oxalate complex.

In purely physical developers, only metal ions and complex metal anions of metals which are more precious than copper, i.e., mercury, silver, platinum, gold or paladium may be used in combination with photographic reducing agents. These metals in the instant application will be hereinafter designated as precious metals. A physical developer frequently used is, for example, a solution of silver nitrate in water to which hydroquinone, metol or p-phenylenediamine has been added. In addition, some further substances are usually added to such a developer, which substances serve to increase the length of life or to control the velocity of development. These are, for example, organic acids, buffer mixtures or substances which enter into reaction with the precious metal salt to form thereby complex metal anions.

The purely physical development hitherto employed has disadvantages which has prevented its general introduction into the photographic techniques. These disadvantages are due to the fact that physical developers, in contradistinction to chemical developers, are unstable systems due to a homogeneous reaction being liable to occur in the solution between the precious metal compound and the reducing agent in addition to the heterogeneous reaction on the latent image, whereby the latter is intensified, which homogeneous reaction then results in the spontaneous formation of metal germs in the solution and in the photographic material outside of the latent image which germs form precipitates. In addition, a spontaneous catalyzed reduction may occur on the wall of the developing vessel and this reduction likewise gives rise to unwanted loss of metal. Once such metal germs having spontaneously been formed, their growth will compete with the deposition of the metal on the latent image obtained by the reaction of light. This spontaneous formation of the metal precipitates, of course, also takes place when the physical developer is not in use and this results in fairly rapid deterioration of such developers while isolating metal and in considerable contamination of the vessels employed. Such developers are thus uneconomical in use.

The spontaneous formation of the metal germs and resultant formation of precipitates in the photographic material outside the latent image obtained by illumination may give rise to unwanted fogging of the ultimate photographic image. The spontaneous dissociation reaction in physical developers is usually accomplished in a period of time which is not very much longer than the time required for the development of the metal latent image into a photographic visual metal image of desired optical density.

It is known that, in certain cases, it is possible to increase the length of life of a purely physical developer, for example, by reducing the temperature, by dilution, by decreasing the pH or by the addition of the oxidation product of the reducing agent. However, these steps cause a corresponding increase in the time of development, thus rendering such processes serviceable for the technique only in certain cases or in combination with additional steps. Such a step is, for example, to increase the temperature of photographic material containing an amount of such a developer sufficient for building up the image. Developers thus treated have sometimes been referred to as "stabilized" developers. However, they are not stabilized in the sense of the present invention in which the spontaneous separation of the precious metal from the developer is likewise materially decreased, but without at the same time considerably retarding the velocity of development. The first-mentioned kind of increase of the length of life will be referred to hereinafter as "inactivation" and the relevant developers will be re-

ferred to as "non-activated developers." If, on the other hand, as if frequently desirable, efforts are made to shorten the time of development in the purely physical development, for example by increasing the temperature, by the use of higher concentrations of the reacting constituents, or by increasing the pH, this is always at the expense of the length of life of the developer, while the possibility of fogging considerably increases, in certain cases even to an extent such that the selectivity of the precipitation of metal on the photographic metal latent image is lost to a considerable proportion.

The drawbacks hitherto inherent in the purely physical development are responsible for the fact that in the photographic process based on the photo-sensitivity of silver halide, the chemical development has been preferred. However, there are cases that chemical development is impossible and hence physical development is the only possibility of intensifying the photographic latent images, since the image-producing metal, in contradistinction to the chemical development, is not yet present as a non-soluble compound at the area of the image. However, also in these cases in which chemical development is possible, physical development is sometimes desirable in view of the better quality of the image, for example, in connection with the high isolating capacity that can be obtained with it.

It is therefore a principal object of this invention to provide purely physical developers which are stable, that is, in which there is little or no precipitation of metal from the precious metal compound in the developer outside of the latent photographic image.

Another object of this invention is to provide purely physical developers which do not cause fogging.

These and other objects of the invention will be apparent from the description that follows.

According to this invention it has been found that the precipitation of the precious metal from the developer outside of the latent image because of the homogeneous reaction between the photographic reducing agent and the precious metal compound of the developer can be eliminated to a very large extent by the addition of one or more suitable ionic surface active agents or surfactants to the developer. As a result of the additional of these surfactants the life of the developer is increased at least 50% and in one case is 10,000 times that of the corresponding unstabilized developer, Example X.

The use of these ionic surfactants is based on the different behaviours of the ionic surfactants in physical development, so far as the metal precipitates spontaneously formed in the developer and the visual metal image in the photographic material are concerned. Such a selectivity is, of course, essential to proper action of the development stabilizers. It is extremely surprising that the said ionic surfactants considerably delay the growth of the metal precipitates spontaneously formed, without nevertheless affecting the growth of the photographic metal visual image in the exposed layer in a manner which is of practical importance.

The process of the invention may be carried out with all those photographic materials in which a physically developable metal latent image may be obtained directly or indirectly by the action of light. These photographic materials include first of all those materials which contain a photo-sensitive compound, the light reaction product of which as such already behaves as a physically developable photographic metal latent image, for example materials containing silver halides as the photo-sensitive compound. In addition, they include all those photographic materials which contain a photosensitive compound the light reaction product of which as such is not physically developable, but by a secondary reaction may be converted or react into a physically developable photographic metal latent image. If the light reaction product is a metal compound, this secondary reaction consists in isolating metal particles from the metal compound,

as is the case, for example, in the photographic process in which use is made of the photo-sensitivity of the so-called Eder solution and in which the light reaction product is mercurous chloride. Numerous photo-sensitive compounds are also known, the light reaction product of which in a secondary reaction may react in the presence of moisture with mercurous-ions or with silver-ions while forming physically developable latent mercury images and latent silver images respectively. Such photo-sensitive compounds, such as aromatic diazonium compounds, diazosulphonates and diazocyanides and inorganic complex compounds, are used in a large number of processes for the manufacture of photographic images.

Surfactants or surface-active substances, that is to say, substances which are adsorbed at the boundary surface of two phases, are usually organic compounds having amphipathic properties. Their molecule or ion contains one or more hydrophobic and one or more hydrophilic groups, which are bonded together either directly or via, for example, an ester, ether or amide bond. The hydrophobic groups are, for example, aliphatic carbon chains having from 8 to 18 carbon atoms with a very small affinity to the medium (water), in contradistinction to the hydrophilic groups which have a great affinity to water. The latter are therefore sometimes referred to as solubilising or polar groups. These may be, for example, sulphonate or pyridinium groups.

The surfactants may chemically be divided into two classes:

(*a*) The ionic surfactants, the hydrophilic group of which carries the charge and which thus occur in the form of an anion, a cation or a "zwitterion." Reference is then made to anion-active, cation-active and amphoteric surfactants, respectively.

(*b*) The non-ionic surfactants, the hydrophilic group of which is non-ionizable.

During the establishment of the present invention, it has been found that a favourable technical effect in the sense previously described can be obtained only when use is made of surfactants of the first-mentioned category that is the ionic surfactants. The non-ionic surfactants are thus unserviceable as development stabilizers. The serviceable surfactants chiefly belong to the classes of the cation-active, anion-active and amphoteric micelle-producing surfactants and to the class of the cation-active macro-molecular surfactants.

In chemical developers, too, surfactants are sometimes used, for example of the quaternary ammonium type compounds. These may considerably speed up the development of various kinds of photographic emulsions in developers of a given composition. This effect occurs when the exposed material, prior to development, is bathed for a short time, for example, in a 0.2% solution of lauryl-pyridinium-p-toluenesulphonate. The problem for which the present invention provides a solution in the physical development does not exist, however, in the chemical development and the effect of the surfactants is therefore of quite a different nature.

As previously mentioned, physical developers may have greatly differing compositions; they may react in an acid, neutral or alkaline reaction and they may contain different compounds of precious metals, photographic reducing agents of different kinds and many sorts of auxiliary materials. Consequently, it will be evident that the choice of the ionic surfactants used for obtaining stabilization of development cannot be arbitrary. For example, those few ionic surfactants which produce in one way or another a precipitation with one of the constituents of the physical developer cannot be used. Also there may be insufficient activity by the surfactant because of the low dissociation of the surfactant at the pH of the developer concerned.

In order to determine whether a given ionic surfactant is serviceable as a physical developer stabilizer under the

conditions which prevail in the physical developer chosen, the following test may be carried out.

By means of a sensitometer wedge, identical photographic metal latent images are manufactured on two foils of one of the photographic materials defined above. In covered developing vessels one of these foils is developed in a developer containing the surfactant to be tested (A), the other foil being developed in the corresponding developer from which this surfactant is omitted (B). The two foils are developed as long as is necessary for obtaining a predominantly neutral-gray copy of the wedge in developer B. In the event of the length of life of developer B being so short as to be incapable of developing into one neutral-grey copy, the development is stopped when the activity of the developer has ceased. After the development of the first two foils has been terminated, new latent image foils identical with the first-mentioned are introduced some more times into the two developers at given intervals, the period of which may naturally be varied as a function of the length of the developers. The lengths of life of the two developers are thus approximately determined, that is to say, the times which elapse between the moment when the two developers were prepared and the moments when their developing power has disappeared almost completely. This test has at the most a semi-quantitative character, since the spontaneous formation of the metal precipitate in non-stabilized developers is naturally not reproducible with great accuracy. In order to avoid wrong conclusions which might result from the said fluctuations, one sets as a criterion of activity that the length of life of developer A with respect to that of developer B must be increased at least by 50%.

During this test it is necessary to ensure that the total amount of image metal which is consumed for building up the image in all the copies of the wedge developed in one and the same developing bath, is not more than 10% of the initial potential supply of metal of this bath.

It is not possible generally to indicate the limits of the effective range of concentration of the surfactants. Most of the surfactants commercially sold are technical products which usually consist of a mixture of homologues which possess the same hydrophilic group and hence are not clearly defined chemically. Otherwise these technical products are, on the whole, quite serviceable without further purification, insofar as they do not show unwanted reactions in the physical developer such as formation of a deposit. However, during the establishment of the invention, it has been found that the number of carbon atoms of the lyophilic group influences the lower limit of activity when starting from pure, well defined compounds. Thus, for example, for a given physical developer it was found that for octylamine acetate this limit exists at a concentration of about 0.1 mol, for decylamine acetate at a concentration of 0.03 molar and with dodecylamine acetate at a concentration of 0.003 molar.

These results indicate that the stabilization effect of the surfactants may be related to micelle formation by the hydrophilic ions of the surfactants at or about the small spontaneous precious metal germs from the precious metal compound thus preventing the germs from growing large enough to precipitate out of the developer solution.

With increasing concentration of the surfactant, the stabilizing effect in certain cases increases, then reaches a maximum and finally disappears completely. The latter is frequently accompanied by flocculation of the surfactant, in which event the activity frequently returns to an increased extent, if the flocculated surfactant is solubilized with another ionic surfactant of the same charge or with a non-ionic surfactant. In other cases, however, a decline in activity upon increasing concentration of the surfactant could not be determined. It is not yet quite clear how all these phenomena must be interpreted. With reference to the sensitometer wedge test described supra, it is possible in all cases to determine the most active concentration or concentrations of the surfactant empirically.

During the experiments carried out in formulating this invention it was found by micro-electrophoretic measurements on the physical developers that the surfactants acted upon the electrophoretic charge of the precious metal germs. In the absence of the surfactants it was found that these previous metal germs had a charge depending to a large extent on the other ingredients in the developer. Thus it was found that the electrophoretic charge of the spontaneous silver germs was distinctly negative in a metol-citric acid-silver nitrate developer and distinctly positive in a corresponding p-phenylene diamine-citric acid-silver nitrate developer. In corresponding alkaline developers in which sodium sulphite was employed in addition the charge on silver germ in both cases was found to be negative. The spontaneously formed germs of mercury were however, found to be positive in a hydroquinone, nitric acid, mercurous nitrate developer.

The surfactants act to increase the existing charge of the precious metal germs or to provide a new strong charge of opposite polarity on the precious metal germ depending on whether cation or anion-active surfactants are employed and whether the charge on the precious metal germ is the same or opposite to that of the hydrophilic ion released by the surfactant. By thus effecting the electrophoretic behaviour of the spontaneously formed precious metal germs in the physical developers the growth of these germs into sizes large enough to precipitate out of the solution is prevented.

The action of the hydrophilic ions on the charge of spontaneous precious metal germs involves probably the formation of micelles which as stated before prevents the growth of these germs. A strong positive charge of the germs will prevent the approach of positive metal ions, whereas a strong negative charge may prevent transmission of electrons to the germs and approach of negative complex metal ions. Consequently, in certain cases, a hydrophilic ion of one type of charge and, in other cases, one of the other type of charge, but frequently hydrophilic ions of both type of charge result in a stabilizing effect in a physical developer. However, the photographic test above described always gives an answer to the question whether a given stabilizer is effective in certain kind of developer.

Nevertheless, it remains a surprising fact that the photographic metal latent image is not acted upon in the same manner as are the germs spontaneously formed, in other words, that any appreciable decrease in the velocity of development does not occur. Evidently, the position is such that formation of micelles does not occur in the latent image and that micelles formed outside latent image cannot enter it.

It has been found that most effective stabilization of the physical developer is ensured, at least if the surfactant chosen does not become inactive due to reaction with one of the constituents of the developer, for example due to formation of a precipitate, if the surfactant is chosen to be such that the charge of the surface-active ion is opposite to the electrophoretic charge of the precious metal germs formed spontaneously in the corresponding physical developer from which the surfactant has been omitted and if the concentration of the surfactant is sufficient so as to be capable of giving the spontaneous metal germs the charge of the surface-active ion.

When use is made of physical developers containing a soluble silver compound, silver germs are often spontaneously formed in a non-stabilized developer having a predominantly negative charge. In accordance with the above mentioned rule, a suitable cation-active surfactant thus permits the obtaining of a proper stabilizing effect. But even if silver germs spontaneously formed in the non-stabilized solution have a predominantly positive charge,

the said surfactants still permit the obtaining of a stabilizing effect, though usually not so highly spectacular.

Anion-active and amphoteric polymeric (macromolecular) surfactants usually have an insignificant effect as development stabilizers. On the contrary, cation-active polymeric surfactants are very serviceable more particularly when use is made of a physical developer containing a soluble silver compound.

When using an acid silver developer a particularly favourable technical effect with regard to stabilization is obtained with the aid of compounds from the following clases of cation-active surfactants:

(*a*) Salts of primary alkylamines, the hydrophobic alkyl alkyl radical of which possesses at least 8 carbon atoms, or mixtures of these compounds;
(*b*) Compounds, the basic, hydrophilic, nitrogen-containing group of which is bonded via an ambide bond with the hydrophobic group;
(*c*) Compounds, the basic, hydrophilic, nitrogen-containing group of which forms part of the morpholine ring system;
(*d*) Compounds, the basic, hydrophilic, nitrogen-containing group of which forms part of a heterocyclic five-membered ring.

When use is made of acid silver developers, alkylaryl sulphonates derivatives of diphenyl also have admirable stabilizing properties.

When using alkaline silver developers, compounds from the following classes of cation-active surfactants have a very favourable stabilizing effect:

(*a*) Compounds, the basic, hydrophilic, nitrogen-containing group of which forms part of a pyridine ring system;
(*b*) Salts of primary alkylamines, the hydrophobic alkyl radical of which possesses at least 8 carbon atoms, or mixtures of these compounds;
(*c*) Compounds, the basic, hydrophilic, nitrogen-containing group of which is bonded through an ether group with the hydrophobic group.

With the last-mentioned type of silver developers, compounds from the following classes of anion-active surfactants are also admirably serviceable as development stabilizers:

(*a*) Salts of sulphuric acid semi-esters of aliphatic alcohols;
(*b*) Alkylaryl sulphonates.

The known method of color forming physical development by means of developers containing a soluble silver compound, in which an image of dye-stuff is obtained in situ with a silver image, yields the same favourable results when use is made of surfactants according to the present invention. In selecting the type of surfactant it is in this case also necessary to make allowance for the acid and alkaline reaction, respectively, of the developer concerned.

In physical developers containing a soluble mercury compound, the use of anion-active stabilizers usually yields optimum results. However, if these developers react alkaline it is also possible to obtain a favorable stabilizing effect with cation-active compounds and more particularly with surfactants having a basic, hydrophilic, nitrogen-containing group which forms part of a pyridine ring system.

A very good stabilizing effect may be obtained in physical development by means of acid reacting developers containing soluble silver compounds or mercury compounds if the reducing agent employed is a compound of the hydroquinone type and the stabilizer is an alkylaryl sulphonate derived from diphenyl.

Finally, physical gold developers may best be stabilized by means of the same alklaryl sulphonates which are derivatives of disphenyl.

As previously mentioned, a given surfactant may sometimes show a considerably smaller stabilizing effect than could be expected due to its being flocculated under the conditions which prevail in the physical developer or due to its having itself unduly low solubility. In this case, the activity of the surfactant may be considerably increased by solubilization. This may be effected by means of another ionic surfactant of the same type or by means of a non-ionic surfactant.

A process is also known for obtaining metallic images in photographic material by purely physical development of photographic metal latent images, the photographic material being developed in the form of a stack of sheets in a physical developer which may be inactivated, if desired, and which contains an amount of metal salt not more than about three times as much as suffices for building up the visual images. According to the invention, by the use of surfactants in the developers, much more beautiful results, less fogging and less contamination of the sheets due to finely-divided metal loosely deposited on them is obtained.

In combination with known steps by which the purely physical development is used in a continuous process, the invention imparts to the developer properties rendering it even much more attractive for practical use.

It is possible to carry out a developing process in which the developing liquid is continuously supplied from two separate supply solutions which are stable in themselves. The invention may then successfully be used by adding a development stabilizer to at least one solution, so that better results are obtained and the process is accomplished more economically.

If a certain amount of photographic material is physically developed several times in succession in a given amount of developer which is stabilized and possibly inactivated, the present invention also permits of regenerating this developing liquid at will by adding metal salt or an aqueous solution thereof which may be provided with a stabilizer. The process of regenerating the developer may, of course, also be carried out continuously.

In addition, the known continuous process in which the photographic material is caused to absorb an amount of inactivated developer at least sufficient for building up the images and in which the development is accomplished substantially outside this supply, may be considerably improved by the use of the invention, since by means of stabilizers it is possible to prepare developer solutions which are durable for a much longer time than are the corresponding non-stabilized solutions and which nevertheless exhibit a reasonable developing activity.

The invention will now be explained in detail with reference to a number of examples.

EXAMPLES

(The specified formulas are included in the accompanying table.)

I. A superficially saponified film of cellulose acetate was sensitized by impregnating for 2 minutes with an aqueous solution containing 0.15 gram mole of the sodium salt of o-methoxy-benzenediazosulphonic acid and 0.1 gram mole of cadmium lactate per liter, followed by wiping off and drying. A piece of this film was exposed to the light of a mercury lamp behind a sensitometer wedge and subsequently treated with an aqueous solution containing 0.005 gram mole of mercurous nitrate and 0.01 mol of nitric acid per liter, resulting in a mercury germ image being formed (the so-called "germ image foil"). After the formation of the germ image, the foil was rinsed in distilled water. A strip of the germ image foil was physically developed for 10 minutes in a fresh solution of 0.5 g. of metol, 2 g. of citric acid and 0.2 g. of silver nitrate in 100 g. of distilled water. The silver germs spontaneously formed in this solution were found to have a negative electrophoretic charge. Another strip of the same germ image foil was

developed for the same period in a fresh solution which, in addition to the said constituents, also contained 0.02 g. of the cation-active sulfactant "Sapamine KW." This is the methyl sulphate of monostearylamido-ethylene-trimethyl-amine (Formula I). It was determined by electrophoretic means that the germs formed spontaneously in the solution had a very distinct positive charge. With certain intervals, which in this case were about 30 minutes, new strips of germ image foils identical with the first-mentioned were introduced into the two developing solutions and developed therein for 10 minutes.

This procedure was continued until the developing power of each solution had disappeared almost completely, while taking care that in total not more than about 10% of the silver potentially present in each of the developers at the beginning of the test was used for building up the image. The stabilized developing solution became inactive in a period of time which was three times as long (the "stabilization factor") as that in which the developer without the stabilizer became inactive. A delay in the development was not established at all in this and the following examples of stabilized physical developers, unless special statements are made to the contrary.

Instead of using the above-mentioned photo-sensitive material, it is alternatively possible in this and the corresponding subsequent examples to utilize similar materials obtained by impregnation of regenerated cellulose film or superficially saponified cellulose-ester film with solutions of other aromatic diazosulphonates such, for example, as the sodium salt of p-methoxy- or p-ethoxy-benzenediazosulphonic acid, the sodium salt of chloro-2-methyl-4 benzenediazosulphonic acid-1, and the sodium salt of dimethoxy-3,4 benzene-diazosulphonic acid-1, or with solutions of other photosensitive compounds from which one or more of the following molecules or ions are released by exposure: CN^-; CNS^-; NO_2^-; $SO_3^=$; SO_2; $S_2O_3^=$; NH_3; pyridine, thiourea or derivatives thereof.

II. A portion of a germ image foil obtained in the manner described in Example I was physically developed for 5 minutes in a fresh aqueous solution containing 0.036 gram mole of hydroquinone, 0.1 mol of nitric acid and 0.005 gram mole of mercurous nitrate per liter. It was determined by electrophoretic means that the mercury germs spontaneously forming in this solution had a positive charge. Another piece of the same foil was developed during the same time in a similar fresh solution containing, in addition, 0.2% by weight of the anion-active surfactant "Aresklene-400" (Formula II), the dibutyl-O-phenylphenolsodium disulphonate. The spontaneous germs in this solution had a distinct negative charge. A portion of a germ image foil identical with the first-mentioned, after having been introduced into the developing solution without the surfactant two hours after the manufacture thereof, could be intensified no longer. On the other hand, in the developer containing the surfactant, strips of identical germ image foils could be intensified into neutral-black images in developer solutions 50 hours old when using a time of development of 5 minutes.

III. A superficially saponified foil of cellulose acetate was sensitized by impregnating for 2 minutes in a 2% by weight solution of anthraquinone disulphonic acid sodium-2,7, followed by wiping off and drying. After exposure of foils of this material to light by means of a mercury lamp, silver germ images were formed by treatment of the foils with an aqueous solution containing per liter 0.01 gram mole of silver nitrate and 0.2 gram mole of a mixture of acetic acid and sodium acetate buffer (pH=6). After this introduction of germs, the foils were rinsed in distilled water for 10 seconds.

The following physical developers were used:

(*a*) An aqueous solution containing 0.027 gram mole of p-phenylene diamine, 0.028 gram mole of silver nitrate and 0.95 gram mole of anhydrous sodium sulphite per liter, and

(*b*) A similar solution containing, in addition, 0.02% by weight of "Fixanol-C" (Formula III), a cetyl pyridinium halide. The time of development was always 30 minutes.

A micro-electrophoretic test revealed that the silver germs spontaneously forming in solution *a* had a negative charge, whereas the spontaneous germs in solution *b* had a distinct positive charge. The length of life of developer *b* was 50 times as long as that of developer *a*.

Instead of using the above-mentioned photo-sensitive material, it is alternatively possible in this and corresponding subsequent examples to utilize similar materials obtained by impregnating at least superficially hydrophilic films with solutions of other photo-sensitive compounds the light reaction product of which is capable of isolating metallic silver from solutions of silver salts, such, for example, as various naphthoquinoni- and anthraquinoni compounds and certain thiazine-, azine- and oxazine dyes.

IV. A superficially saponified foil of cellulose-triacetate was sensitized by impregnating for 2 minutes in an aqueous solution containing 0.4 gram mole of hydroxy-1 diazo-2 methyl-6 benzenesulphonic acid-4, 0.05 gram mole of mercurous nitrate and 0.1 gram mole of nitric acid per liter. After drying and exposure behind a sensitometer wedge with the aid of a mercury lamp, the foil was rinsed in distilled water for a short time, resulting in a mercury germ image being formed. Portions of the germ image foil thus obtained were physically developed for 10 minutes in the following freshly prepared solutions:

(*a*) A solution of 0.5 g. of metol, 2 g. of citric acid and 0.2 g. of silver nitrate per 100 g. of distilled water;

(*b*) Solution *a*+0.02% by weight of "amine 220" nitrate (Formula V); this is hydroxyethyl-1 heptadecenyl-2 imidazolinium nitrate;

(*c*) Solution *a*+0.02% by weight of "amine-O" acetate (Formula IV); this is, as the Amine-220, a compound, the basic hydrophilic, nitrogen-containing group of which forms part of an imidazoline ring system.

(*d*) Solution *a*+0.02% by weight of "Sapamine A" (Formula VI); this is a compound the basic, hydrophilic, nitrogen-containing group of which is bonded via an amide bond with the hydrophobic group;

(*e*) Solution *a*+0.04% by weight of the acetate of "Ethoduomene T/13" (Formula VII); this is a ditertiary amine;

(*f*) Solution *a*+0.2% by weight of "Desogene" (Formula VIII); this is a quaternary ammonium compound.

Upon repeating the test in the same developer, the solution *b* to *f* were found to have a length of life which was from an 1½ to 3 times longer than that of solution *a*.

Instead of using the above-mentioned sensitizing solution, it is alternatively possible, for example to utilize a solution containing 3 g. of hydroxy-1 diazonium-2 naphthalene-sulphonic acid-4,2 g. of citric acid and 4 g. of silver nitrate per 100 g. of water. Exactly the same results are obtained with germ image foils of this material.

V. A superficially saponified foil of cellulose triacetate was sensitized by impregnating for 2 minutes in an aqueous solution containing per liter 0.07 mol of the sodium salt of p-methoxy-benzene diazosulphonic acid and 0.07 gram mole of cadmium acetate per liter, followed by drying. After a sensitometer exposure by means of a mercury lamp, a treatment followed for 2 seconds with an aqueous solution containing 0.005 gram mole of mercurous nitrate and 0.01 gram mole of nitric acid per liter, so that the mercury germ image was introduced. This was followed by rinsing in distilled water for 10 seconds.

A portion of the resultant germ image foil was physically developed for 7 minutes in a freshly prepared aqueous solution containing 2% by weight of pyrogallol, 2% by weight of citric acid and 0.2% by weight of silver nitrate. Another portion of the same germ image foil was developed at the same time and for the same period in a solution prepared in the same manner and containing, in addition, 0.2% by weight of the polymeric cation-active surfactant polyvinyl-imidazol quaternized with methyl sulphate (Formula IX).

The developing tests described were repeated with strips of other germ image foils identical with the first-mentioned at intervals of 15 minutes, until the developing power of the developers had disappeared almost completely. The developer stabilized by the polymeric surfactant was found to have a length of life three times longer than that of the non-stabilized developer.

When use is made of developers which, instead of pyrogallol, contain 0.5% by weight of metol and 0.2% by weight of N,N-dimethyl-p-phenylene diamine nitrate, respectively, but are otherwise prepared in a similar manner as above, corresponding increases in the lengths of life of the relevant developers are obtained by means of the said polymeric surfactant.

VI. A strip of a germ image foil obtained in the manner described in Example V was physically developed for 5 minutes in an aqueous solution containing per liter 0.05 gram mole of ferrous sulphate, 0.005 mol of ferric nitrate, 0.14 gram mole of citric acid and 0.006 gram mole of silver nitrate. Three other strips of the same germ image foil were developed simultaneously and during the same time in solutions prepared in a similar manner and containing, in addition, 0.02% by weight of

(*a*) "Armac 12 D" (Formula X);
(*b*) "Aerosol C 61"(American Cyanamid Co.), an ethanolated alkyl guanidine compound;
(*c*) "Deodorant G 271" (Formula XI), a compound, the basic, hydrophilic, nitrogen-containing group of which forms part of a morpholine ring system;
(*d*) The nitrate of "Amine-S" (Formula V), a compound, the basic, hydrophilic, nitrogen-containing group of which forms part of an imidazoline ring system.

The length of life of each developer was determined in the manner specified in the description of the invention. It was found that, due to the addition of the said four cation-active surfactants, stabilization occurred by a factor which varied between about 2 and 15.

When working in an otherwise similar manner with developing solutions containing 0.02% by weight of the reducing agent phenyl-1 pyrazolidon-3 ("Phenidone"), 2% by weight of citric acid and 0.02% by weight of silver nitrate, the said four surfactants brought about stabilization by a factor which varied between about 2 and 10.

VII. The stabilizing effect of the cation-active surfactants (already used in concentrations of 0.02% by weight) "Sapamine KW" (Formula I; see also Example I) and "Deodorant G 271" (Formula XI; see also Example VI) was tested in physical developers of the following compositions:

(*a*) 2% by weight of hydroquinone, 2% by weight of citric acid and 0.2% by weight of silver nitrate (time of development: 15 minutes);
(*b*) 2% by weight of pyrogallol, 2% by weight of citric acid and 0.2% by weight of silver nitrate (time of development: 5 minutes);
(*c*) 2% by weight of pyrocatechol, 0.5% by weight of citric acid and 0.2% by weight of silver nitrate (time of development: 20 minutes);
(*d*) 0.25% by weight of o-aminophenol, 2% by weight of citric acid and 0.2% by weight of silver nitrate time of development: 15 minutes);
(*e*) 0.125% by weight of p-aminophenol, 1% by weight of citric acid and 0.05% by weight of silver nitrate (time of development: 10 minutes);
(*f*) 0.06% by weight of N-p-hydroxyphenylglycine ("Kodurol"), 2% by weight of citric acid and 0.05% by weight of silver nitrate (time of development: 7 minutes);
(*g*) 0.21% by weight of N,N-diethyl - p - phenylenediamine nitrate, 2% by weight of citric acid and 0.2% by weight of silver nitrate (time of development: 7 minutes).

Use was made of germ image foils obtained in the manner described in Example I. The lengths of life of the developers, stabilized and unstabilized, were determined in the manner specified in the description. The length of life of the stabilized developers varied from 1.5 to 3 times that of the unstabilized developers.

VIII. The stabilizing effect of the cation-active surfactants:

(*a*) "Almac 26 D" (General Mills Inc.), a mixture of oleyl-, palmityl- and stearylamino-acetates and
(*b*) "Deodorant G 271 (Formula XI), used in concentrations of 0.02% by weight, was tested in a physical developer containing 0.25 g. of ascorbic acid, 2 g. of citronic acid and 0.06 g. of silver nitrate per 100 g. of water. Germ image foils obtained, for example, in the manner described in Example I, were developed into substantially neutral-gray images within 10 minutes.

The surfactants *a* and *b* increased the length of life of this developer by a factor 6 and a factor 2, respectively.

IX. Filter paper was sensitized, exposed and, subsequently, a mercury germ image was introduced in the manner described in Example I.

A strip with the germ image was physically developed for 10 minutes in a freshly prepared aqueous solution containing 0.1% by weight of metol, 0.42% by weight of citric acid and 0.05% by weight of silver nitrate. Other strips with identical germ images were developed during the same time in solutions prepared in the same manner and containing, in addition, 0.02% by weight of "Sapamine KW" (Formula I) and "Deodorant G251" (Formula XII) respectively. Strips with germ images produced by the first-mentioned method were developed simultaneously in the stabilized and the non-stabilized developing solutions at intervals of half an hour. The increase in the length of life of the developer as a result of the addition of the stabilizers was a factor 2 to 3.

Instead of germ images in filtration papers, such images obtained in unilaterally sensitized, white litho-paper free of wood could also be used with similar result.

X. Germ image foils obtained on the photo-sensitive material and by means of the germ forming process described in Example III, were used for testing the stabilization of an alkaline physical developer of the following composition: 0.38% by weight of "Genochrome"; this is the p-N,N-diethyl-amino-aniline sulphite complex, 6.2% by weight of anhydrous sodium sulphite and 0.5% by weight of silver nitrate in distilled water. The effect was tested of the following additions of cation-active surfactants:

(*a*) 0.014% by weight of "Fixanol C" (Formula III), a compound, the basic, hydrophilic, nitrogen-containing group of which forms part of a pyridine ring system.
(*b*) 0.014% by weight of "Armac 12D" (Formula X), a primary dodecyl-amine acetate;
(*c*) 0.014% by weight of "Hyamine 10 X" (Formula XIII), a compound, the basic, hydrophilic, nitrogen-containing group of which is bonded through an ether bond with the hydrophobic group.

The method of testing which was adopted has been mentioned in detail in the general part of the description. The time of development was always 2 minutes.

The solution which did not contain a surfactant was found to have lost its developing power already after a

few minutes. With the use of surfactant *a*, the length of life of the developer was about 1 hour, with the use of surfactant *b* it was about 250 hours, and with the use of surfactant *c* it was about 5 hours. In the case *a*, a small delay in development was found.

XI. With the aid of the germ image foils also used in Example X, and with the use of an alkaline physical developer containing per liter 0.014 gram mole of hydroquinone, 0.95 gram mole of anhydrous sodium sulphite and 0.0146 gram mole of silver nitrate (time of development 8 minutes), the stabilizing effect was tested of additions of 0.014% by weight of the following surfactants:

(*a*) Cetyl pyridinium bromide (Formula III) wherein X=Br;
(*b*) "Armac 12 D" (Formula X);
(*c*) "Aerosol C 61" (see Example VI).

The lengths of life of the developers containing the said surfactants were 3, 100 and 2 times, respectively, longer than the length of life of the developer without a stabilizer.

XII. A strip of a germ image foil manufactured as described in Example I was developed for 7 minutes in a freshly prepared aqueous solution containing 0.06% by weight of N-p-hydroxyphenyl glycine ("Kodurol"), 2% by weight of citric acid and 0.05% by weight of silver nitrate. Three other strips of the same germ image foil were developed at the same time, likewise for 7 minutes, in developers prepared in a similar manner and containing, in addition, 0.02% by weight of

(*a*) "Areskap-100" (Formula XIV); this is mono-butyl-phenylphenolsulphonic acid sodium;
(*b*) "Aresket-300" (Formula XV), this is mono-butyl-diphenylsulphonic acid sodium;
(*c*) "Aresklene-400" (Formula II, see also Example II).

By repeating the above-mentioned tests with strips of new germ image foils identical with the first-mentioned after 15, 30, 60 and 120 minutes, it was found that these anion-active surfactants had a stabilizing effect corresponding to an increase in length of life by a factor 4.

XIII. The activity of "Aresklene-400" (Formula II) as a development stabilizer was also tested for the following series of acid physical developers:

(*a*) The ascorbic acid developer of Example VIII containing 0.02% by weight of the surfactant;
(*b*) The o-aminophenol developer of Example VII*d* containing 0.2% by weight of the surfactant;
(*c*) The p-aminophenol developer of Example VII*e* containing 0.2% by weight of the surfactant;
(*d*) The metol developer of Example I containing with 0.2% by weight of the surfactant;
(*e*) The phenyl-1-pyrazolidon-3 developer of Example VI containing 0.2% of the surfactant;
(*f*) The o-phenylene diamine-developer of the following composition:
0.2% by weight of o-phenylene diamine nitrate,
2% by weight of citric acid,
0.2% by weight of silver nitrate and
0.2% by weight of surfactant (time of development: 7 minutes);
(*g*) The diethyl-p-phenylene diamine developer of Example VII*g* containing 0.02% by weight of the surfactant;
(*h*) The ferrous-developer of Example VI, likewise containing 0.02% by weight of the surfactant.

The lengths of life of all these developers were from 2 to 8 times as long as that of the corresponding non-stabilized developers. The development of germ foils in these developers was free of fogging effect, whereas the development in the non-stabilized developers sometimes involved troublesome fogging.

XIV. The stabilizing effect of a plurality of anion-active surfactants belonging to the classes of the salts of sulphuric acid semi-esters of aliphatic alcohols and of the alkylaryl sulphonates was tested for the following alkaline physical developers:

(*a*) The alkaline hydroquinone developer of Example XI;
(*b*) The alkaline p-methylaminophenolsulphate (metol) developer of the composition:
Metol: 0.014 molar
Anhydrous sodium sulphite: 0.95 molar
Silver nitrate: 0.0146 molar
Time of development: 8 minutes
(*c*) The alkaline N,N - diethylamino - anilinesulphite ("Genochrome") developer of the compositon:
"Genochrome": 0.0157 molar
Anhydrous sodium sulphite: 0.95 molar
Silver nitrate: 0.0295 molar
Time of development: 2 minutes

The following surfactants were used:

(1) 0.014% by weight of "Lissapol C" (Formula XVI) in the developers *a*, *b* and *c*. Stabilization factor: 4 to 10;
(2) 0.15% by weight of "Areskap-100" (Formula XIV, see also Example XII) in developer *a*. Stabilization factor: 2;
(3) 0.14% by weight of "Aresket-300" (Formula XV, see also Example XII) in developer *a*. Stabilization factor: 2;
(4) 0.14% by weight of "Aresklene-44" (Formula II, see also Example II) in the developers *a* and *b*; 0.014% by weight of "Aresklene-400" in developer *c*. Stabilization factor: 5 to 20.
(5) 0.014% by weight of "Nekal BX," an alkylaryl sulphonate, in the developers *a* and *b*. Stabilization factor: 3 to 8.

If, in the last-mentioned case, one of the alkylaryl sulphonates "Invadin N" or "Perminal BX" instead of "Nekal BX" was used, stabilizing effects were obtained which were likewise very acceptable.

XV. With the aid of germ image foils obtained in the manner described in Example III, tests were carried out on an acid developer and an alkaline color forming physical developer, in order to determine to what extent the lengths of life of these developers can be increased by the use of ionic surfactants.

The compositions and the times of development of the relevant developers were as follows:

(*a*) 0.2% by weight of p-N,N-dimethylamine-aniline nitrate, 2% by weight of citric acid, 0.2% by weight of silver nitrate, and 0.08% by weight of α-naphthol (coloring component) in distilled water. Time of development: 1.5 minutes.

(*b*) The "Genochrome"-developer of Example X, to which 0.11% by weight of phenyl-1 methyl-3 pyrazolon-5 was added as a color forming component. Time of development: 6 minutes.

In developer *a*, the following cation-active surfactants produced the stabilizing effects mentioned therewith:

0.02% by weight of "Armac 12D" (Formula X), stabilization factor: 20;
0.02% by weight of "Sapamine KW" (Formula I), stabilization factor: 5;
0.02% by weight of the nitrate of "Amine-S" (Formula V), stabilization factor: 5;

In developer *b*, the stabilization effects, obtained with several cation-active and anion-active compounds were as follows:

0.014% by weight of "Armac 12D" (Formula X), stabilization factor: 250;
0.014% by weight of cetylpyridinium chloride (Formula III), stabilization factor: 250;
(wherein X=Cl)
0.014% by weight of "Hyamine 10X" (Formula XIII), stabilizaton factor: 20;

0.014% by weight of "Lissapol C" (Formula XVI), stabilization factor: >2;
0.014% by weight of "Aresklene-400" (Formula II), stabilization factor: >2;
0.014% by weight of "Invadin N" (see Example XIV), stabilization factor: >2.

XVI. In a similar manner and with the aid of similar germ image foils as in the preceding example the stabilizing effect of a plurality of anion-active surfactants was tested for several acid and alkaline mercury developers.

Compositions of the developer without stabilizers:

(*a*) Acid hydroquinone developer: see Example II;
(*b*) Acid metol developer:
p-Methylaminophenolsulphate (metol): 0.012 molar
Nitric acid: 0.1 molar
Mercurous nitrate: 0.005 molar
Time of development: 5 minutes
(*c*) Acid N,N-dimethyl-p-phenylene diamine-developer:
N,N-dimethyl-p-phenylene diamine-nitrate: 0.01 molar
Lactic acid: 0.02 molar
Mercurous nitrate: 0.001 molar
Time of development: 3 minutes
(*d*) Alkaline hydroquinone-developer:
Hydroquinone: 0.03 molar
Anhydrous sodium sulphite: 0.45 molar
Mercuric bromide: 0.0145 molar
Time of development: 10 minutes
(*e*) Alkaline metol-developer:
p-Methylamino phenolsulphate (metol): 0.03 molar
Anhydrous sodium sulphite: 0.45 molar
Mercuric bromide: 0.0145 molar
Time of development: 10 minutes
(*f*) Alkaline N,N-dimethyl-p-phenylene diamine-developer:
N,N-dimethyl-p-phenylenediamine nitrate: 0.004 molar
Potassium thiocyanate: 0.008 molar
Borax: 0.05 molar
Mercuric bromide: 0.0017 molar
Time of development: 1.5 minutes

The table below gives an impression of the increased length of life of several developers due to the addition of the specified anion-active substances.

Surfactant	Concentration in the developer, percent by weight	Used in developer	Stabilization factor
"Lissapol-C" (Formula XVI)	0.02	a	50
	0.02	b	2
	0.02	f	5
"Aresklene-400" (Formula II)	0.02	b	10
	0.02	c	20
	0.02	d	100
	0.02	e	6
	0.02	f	4
"Perminal-BX"	0.02	a	250
	0.02	b	10
	0.02	c	10
	0.02	d	40
	0.02	e	4
	0.02	f	2

XVII. Some further tests were carried out to determine the stabilizing effect of cation-active surfactants in alkaline mercury developers. These developers, apart from the surfactant, had the following compositions:

(*a*) The alkaline hydroquinone developer of Example XVI*d*;
(*b*) The alkaline metol developer of Example XVI*e*;
(*c*) The alkaline N,N-dimethyl-p-phenylene diamine developer:
N,N-dimethyl-p-phenylene diamine: 0.025 molar
Potassium thiocyanate: 0.046 molar
Borax: 0.05 molar
Mercuric bromide: 0.0097 molar
Time of development: 2 minutes

The surfactants employed and the results were as follows:

Surfactant	Concentration in the developer, percent by weight	Used in developer	Stabilization factor
"Armac 12D (Formula X)	0.02	b	6
Cetylpyridinium bromide (Formula III) wherein X=Br.	$ 0.02	a	12
	$ 0.02	b	8
"Hyamine 10X" (Formula XIII)	0.02	c	2
"Aerosol C61" (see Example VI)	0.02	c	3
"Deodorant G 271" (Formula XI)	0.02	c	2
Nitrate of "Amine-S" (Formula IV).	0.02	a	3
"Quaternary S" [1]	0.02	c	2

[1] Quaternary S in a quaternary imidazolinium chloride, derived from amine-S (Formula IV) having a molecular weight of 455.

For these tests use was made of photo-sensitive material manufactured by impregnating a superficially-saponified foil of cellulose acetate for 2 minutes in a solution containing 5 gms. of mercuric chloride, 5 gms. of ferric ammonium oxalate and 2.5 gms. of ammonium oxalate per 100 gms. of distilled water.

XVIII. Use was made of acid developers of the "hydroquinone" type, in which the alkylaryl sulphonates which are derivatives of diphenyl produced very special effects dependent upon concentration, as may appear from comparison of the results given below and those of Example II on the one hand with those of the Examples XII and XIII, on the other hand.

Developers:
(*a*) Acid hydroquinone developer of Example VII*a*;
(*b*) Acid pyrogallol developer of Example VII*b*;
(*c*) Acid pyrocatechol developer of Example VII*c*.

The stabilizer used was "Aresklene-400" (Formula II).

Concentration in the developer	Developer	Stabilization factor
0.02	a	8
0.2	a	>100
0.02	b	6
0.2	b	>100
0.02	c	4
0.2	c	about 100

XIX. Germ image foils obtained in the manner described in Example I, after having been rinsed in distilled water for 1 minute, were treated with 0.8 molar ammonia and again rinsed in distilled water. Subsequently, the physical development took place for 8 minutes in solutions containing per 100 g. of distilled water:

(*a*) 0.33 g. of potassium gold chloride
1.3 g. of oxalic acid
(*b*) As *a* and, in addition, 0.2 g. of "Aresklene-400" (Formula II).

The length of life of developer *b* was at least twice as long as that of developer *a*.

XX. A strip of a germ image foil obtained in the manner described in Example I, was physically developed for 10 minutes in a freshly prepared solution containing 0.5 g. of metol, 2 g. of citric acid and 0.2 g. of silver nitrate per 100 g. of distilled water. Another strip of the same germ image foil was developed in a similar solution which contained, in addition, 0.02% by weight of "Alamac 26D" (Example VIII*a*) and 0.02% by weight of "Sapamine KW" (Formula I). "Alamac 26D" produced flocculation if added alone to the said metol-citric acid-silver nitrate developer. However, this cation-active surfactant was solubilized by the "Sapamine KW" which is likewise cation-active. The stabilizing effect became manifest by an increase in the length of life of the de-

veloper by a factor of 40. "Sapamine KW" alone produced an increase by a factor 3 only, whereas "Alamac 26D" in the flocculated state did not produce any effect.

XXI. In the tests now following, use was made of germ image foils obtained by exposure of a film specially made for electron microscopy with an emulsion of silver halide. After physical development, the foils were fixed in an aqueous solution containing 5% by weight of sodium thiosulphate and 0.5% by weight of sodium hydroxide, and rinsed.

Efforts were made to stabilize the metol-citric acid-silver nitrate-developer of the preceding example with the use of 0.02% by weight of "Armac 12D" (Formula X). However flocculation then occurred in the developer. Such flocculation could be avoided by adding, in addition, 0.02% by weight of the non-ionogenous compound "Lissapol-N," which as such did not produce any stabilizing effect. However, the combination of the two surfactants produced a stabilizing effect of a factor 10.

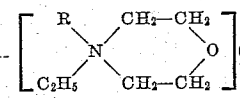
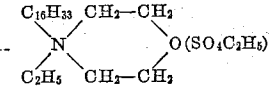
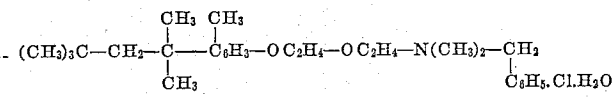
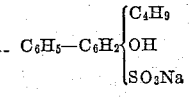
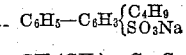
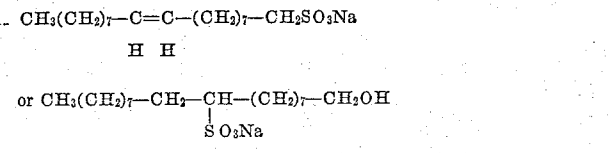
XXII. A strip of a germ image foil manufactured in the manner described in Example I, was developed for 5 minutes in a freshly prepared aqueous solution containing 0.06% by weight of N-p-hydroxyphenyl glycine, 2% by weight of citric acid and 0.1% by weight of silver nitrate. Two other strips of the same germ image foil were developed at the same time, likewise for 5 minutes, in similar fresh solutions containing, in addition, 0.098% by weight of pure dodecyl-amine acetate and 0.098% by weight of pure dodecylamine acetate together with 0.0087% by weight of pure decylamine acetate, respectively. The said surfactants were obtained in the pure state by distilling the free impure amines at decreased pressure in an apparatus having a high separating capacity and subsequently adding the calculated amount of acetic acid to the constantly-boiling fraction. The above-mentioned development tests were repeated in the same solutions after 10, 20, 40, 80 and 160 minutes. In the solution containing only the pure dodecylamine acetate as a surfactant, flocculation was found to occur after 10 to 30 minutes. The stabilizing effect in this solution was comparatively low and non-reproducible, that is to say, dependent upon the time after which the flocculation was largely accomplished. In the solution containing both dodecyl acetate and decylamine acetate, flocculation still occurred after several hours and the stabilizing effect was greater than a factor 10, whereas decylamine, if it was present in the developer as the only surfactant in the concentration used herein, still had not perceptible influence upon stabilization.

XXIII. A strip of a germ image foil obtained in the manner described in Example III, was physically developed in the alkaline hydroquinone developer of Example XI which was freshly prepared and non-stabilized. Another strip of the same germ image foil was developed in the corresponding stabilized developer containing as the stabilizer 0.014% by weight of the amphoteric compound N-lauryl (aminosulpho) β-aminobutyric acid ("Desil"). After every 15 minutes, new germ image foils identical with the first-mentioned were developed in the two developers. The stabilization factor under the described conditions was about 5.

Table

	Formula	Trade Name	Source
I	$[C_{18}H_{37}C(=CH)-NC_2H_4N(CH_3)_3](SO_4CH_3)$	Sapamine KW	Ciba.
II	$C_6H_5-C_6H_2(OH)(SO_3Na)_2(C_4H_9)_2$	Aresklene 400	Monsanto Chem. Co.
III	$(C_5H_5NH-C_{16}H_{33})X$ (X=Cl or Br)	Fixanol C	Light and Co. Imperial Che. Ind.
IV	$CH_3-(CH_2)_n-C(=N-CH_2)-N(R)-CH_2$		
	For Amine O, n=16 Mol. weight=355 For Amine S, n=16 Mol. weight=360 R is a substituent having a comparatively low molecular weight.)	Amine O Amine S	Alrose Chem. Co.
V	$C_{17}H_{33}C(=N-CH_2)-N(CH_2-CH_2OH)-CH_2 \cdot HNO_3$	Amine 220 nitrate	Union Carbide and Carbon Corp
VI	$C_{17}H_{33}C(=O)-NH-C_2H_4N(C_2H_5)_2.CH_3COOH$	Sapamine A	Ciba.
VII	$C_{18}H_{37}N(CH_2-CH_2-CH_2-N(CH_2-CH_2OH)_2)(CH_2-CH_2OH)$	Ethoduomene T/13	Armour and Co.
VIII	$[CH_3-C_6H_4-CH(N(CH_3)_3)-(CH_2)_{10}-CH_3](SO_4CH_3)$	Desogen	Geigy.
IX	$\ldots -CH(N=CH-NH=CH)-CH_2-CH(N=CH-NH=CH)-CH_2-\ldots$	Polyvinylimidazol	Bad. Anilin u. Sodafabr.
X	90% $C_{12}H_{25}-NH_2.CH_3COOH$ 9% $C_{14}H_{29}-NH_2.CH_3COOH$	Armac 12L	Armour and Co.

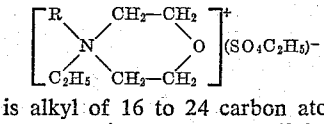
Table—Continued

Formula	Trade Name	Source
XI.  (R=$C_{16}H_{33}$, $C_{18}H_{31}$, $C_{18}H_{33}$, $C_{18}H_{35}$, $C_{18}H_{37}$ and alkyl residues with 20–24 carbon atoms.)	Dedorant G 271	Atlas Powder Co.
XII. 	Deodorant G 251	Atlas Powder Co.
XIII. 	Hyamine 10X	Rohm and Haas.
XIV. 	Areskap 100	Monsanto Chem. Co.
XV. 	Aresket 300	Monsanto Chem. Co.
XVI. 	Lissapol C	Imp. Chem. Ind.

While we have described our invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as defined in the appended claims.

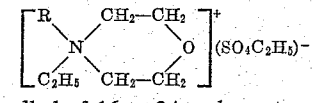
What is claimed is:

1. A stabilized photographic physical developer comprising an acid aqueous solution of a water soluble silver salt reducible to metallic silver, a photographic reducing agent for reducing said silver salt to silver and at least one cationic surfactant said cationic surfactant being selected from the group consisting of water soluble salts of primary alkylamines wherein the alkyl moiety is hydrophobic and contains at least 8 carbon atoms, cetyl pyridinium halides, the methyl sulphate of monostearylamidoethylene-trimethyl-amine, imidazolidine derivatives containing an alkyl of 16 carbon atoms attached to a carbon atom of the heterocyclic nucleus and a lower alkyl attached to a nitrogen of the heterocyclic nucleus, tolylundecylammonium compounds, benzyldimethyl {2{2-[4(Cl,1,3,3 - tetramethylbutyl) tolyloxy]-ethoxy}ethyl} ammonium compounds, N-lauryl (aminosulpho) β-aminobutyric acid, trimethyl-2-oleoylamino-ethyl ammonium compounds, trimethyl-2-stearylamino-ethyl ammonium compounds and morpholine compounds of the formula



wherein R is alkyl of 16 to 24 carbon atoms, said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

2. A stabilized photographic physical developer comprising an acid aqueous solution of a water soluble silver salt reducible to metallic silver, a photographic reducing agent selected from the group consisting of N-methyl-aminophenol sulfate, pyrogallol, N,N-dimethyl-p-phenylene diamine, phenyl-1-pyrazolidone-3, hydroquinone, pyrocatechol, O-aminophenol, p-aminophenol, ascorbic acid, N-p-hydroxyphenylglycine, N-N-diethyl-p-phenylene diamine and a mixture of ferrous and ferric ions for reducing said silver salt to silver and at least one cationic surfactant said cationic surfactant being selected from the group consisting of water soluble salts of primary alkylamines wherein the alkyl moiety is hydrophobic and contains at least 8 carbon atoms, cetyl pyridinium halides, the methyl sulphate of monostearylamidoethylene-trimethyl-amine, imidazolidine derivatives containing an alkyl of 16 carbon atoms attached to a carbon atom of the heterocyclic nucleus and a lower alkyl attached to a nitrogen of the heterocyclic nucleus, tolylundecylammonium compounds, benzyldimethyl {2{2-[4(Cl,1,3,3-tetramethylbutyl) tolyloxy] - ethoxy}ethyl} ammonium compounds, N-lauryl (aminosulpho) β-aminobutyric acid, trimethyl - 2 - oleoylamino-ethyl ammonium compounds, trimethyl - 2-stearylamino-ethyl ammonium compounds and morpholine compounds of the formula



wherein R is alkyl of 16 to 24 carbon atoms, said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

3. A stabilized photographic physical developer comprising an acid aqueous solution of a water soluble silver salt reducible to metallic silver, a photographic reducing agent for reducing said silver salt to silver and at least one anionic surfactant, said anionic surfactant being selected from the group consisting of alkylarylsulfonates and sulfonated alkyl alcohols, said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

4. A stabilized photographic physical developer comprising an acid aqueous solution of a water soluble silver salt reducible to metallic silver, a photographic reducing agent selected from the group consisting of N-methylaminophenyl sulfate, pyrogallol, N,N-dimethyl-p-phenyl diamine, phenyl-1-pyrazolidone-3, hydroquinone, pyrocatechol, o-aminophenol, p-aminophenol, ascorbic acid, N - p-hydroxyphenylglycine, N-N-diethyl-p-phenylene diamine and a mixture of ferrous and ferric ions for reducing said silver salt to silver and at least one anionic

surfactant, said anionic surfactant being selected from the group consisting of alkylarylsulfonates and sulfonated alkyl alcohols, said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

5. A stabilized photographic physical developer comprising an alkalinic aqueous solution of a water soluble silver salt reducible to metallic silver, a photographic reducing agent for reducing said silver salt to silver and at least one cationic surfactant selected from the group consisting of the water soluble salts of cetylpyridinium halides, primary alkylamines wherein the alkyl moiety is hydrophobic and contains at least 8 carbon atoms, benzylmethyl{2{ - [4(Cl,1,3,3 - tetramethylbutyl) tolyloxy]ethoxy}ethyl} ammonium compounds and ethanolated alkyl compounds, said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

6. A stabilized photographic physical developer comprising an alkalinic aqueous solution of a water soluble silver salt reducible to metallic silver, a photographic reducing agent selected from the group consisting of p-phenylene-diamine, p-N,N-diethylamino-aniline sulfite, hydroquinone and N-methylaminophenolsulphate and an alkylaryl sulfonate surfactant said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

7. A stabilized photographic physical developer comprising an alkalinic aqueous solution of a water soluble silver salt reducible to metallic silver a photographic reducing agent for reducing said silver salt to silver and at least one anionic surfactant selected from the group consisting of alkylaryl sulfonates and water soluble salts of sulfuric acid semi-esters of aliphatic alcohols, said surfactant being present in an amount sufficient to increase the life of the developer at least 50% when compared to the life of an identical developer without said surfactant.

References Cited in the file of this patent

UNITED STATES PATENTS

2,000,353	Schaeffer	May 7, 1935
2,197,809	McQueen	Apr. 23, 1940
2,220,929	Kirby	Nov. 13, 1940
2,648,604	Welliver et al.	Aug. 11, 1953
2,662,822	Land	Dec. 15, 1953
2,868,643	Jonge et al.	Jan. 13, 1959

FOREIGN PATENTS

157,182	Australia	June 28, 1951
167,781	Australia	June 17, 1954

OTHER REFERENCES

Glasstone, S.: Physical Chemistry (2d ed.), page 1205, D. Van Nostrand, New York (1954).

Henney and Dudley: Handbook of Photography, pages 346, 373, Whittlesey (McGraw-Hill), New York (1939).

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,157,502 November 17, 1964

Hendrick Jonker 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 7, line 12, for "clases" read -- classes --; line 14, strike out "alkyl"; columns 17 and 18, in the Table, Formula "I" should appear as shown below instead of as in the patent:

$$\left[C_{18}H_{37}\underset{\underset{O}{\|}}{C}\text{-}NC_2H_4N(CH_3)_3\right](SO_4CH_3)$$

same table, under the column headed "Trade Name" opposite formula X, for "Armac 12L" read -- Armac 12D --; column 20, line 71, for "phenyl diamine" read -- phenylene diamine --; column 21, line 15, for "benzylmethyl{2{-[4" read -- benzyl-dimethyl{2{2-[4 --.

Signed and sealed this 3rd day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents