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COMBINED DEVELOPER AND FIXER

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This invention relates to chemical compositions for the combined developing and fixing of silver halide photographic emulsions.

My invention is an improvement on the invention disclosed and claimed in the co-pending application of Goldhammer and Maurer, Serial No. 410,426, filed concurrently herewith. This co-pending application discloses combined developing and fixing compositions in which diaminophenol hydrochloride, commonly known as amidol, or any one of a number of developing agents described in the research literature which have properties similar to those of amidol, and which for convenience may be referred to as developing agents of the amidol type, is used in combination with one or more of the three dihydroxy-benzenes, (pyrocatechol, resorcinol, or hydroquinone), an alkali, a fixing agent, an anti-fogging agent, and an inorganic reducing agent such as sodium sulfite. The developing agents of the amidol type enumerated in the above identified application are 2,4 diaminophenol (amidol); 2,4 diamino-resorcinol; 6-methyl 2,4, diaminophenol; 5-methyl 2,4, diaminophenol; 4-amino - 6 - methyl - 2 - methylamino-phenol; 6-amino-4-methyl - 2 - methylamino - phenol; 5 dimethylamino - 2 - methylamino-phenol; 1,2,4, triaminobenzene; 5-methyl 1,2,4 triaminobenzene; 4 hydroxy: 2′ 4′ diaminodiphenylamine; 4 : 2′ 4′ triaminodiphenylamine; and 1,3, diamino 4,6 dihydroxybenzene. An additional developing agent of a type which has substantial density building action and low fogging action, such as para-hydroxyphenyl glycin or one of the halogen compounds of hydroquinone, may be incorporated with advantage in most applications of the invention.

Baths compounded in accordance with the aforesaid invention of Goldhammer and Maurer have high photographic activity, that is to say, they complete their action in relatively short periods of time (ranging from 3 to 6 minutes) and they produce images of desirably high density and contrast from photographic materials that have received no more exposure than is normal for conventional processing in separate developing and fixing baths.

It is a major advantage of the Goldhammer and Maurer invention that this high level of activity is attained with relatively low values of alkalinity. For example, the prior art formulas of Keelan, given in Photographic Engineering, vol. 4, No. 3 (Formulas 315 and 348) and of Ham, given in U. S. Patent No. 2,230,977 (Examples 1 and 2), which are among the most active compositions previously disclosed, have pH values ranging from 11.0 to 11.55, whereas baths of comparable activity disclosed in the aforesaid Goldhammer and Maurer application have pH values in the range from 8.0 to 9.5.

Primarily because they are only moderately alkaline, the baths disclosed in the Goldhammer and Maurer application have numerous practical advantages over the comparably active baths of the prior art. They do not cause skin irritation, whereas baths having pH of the order of 11.0 can be employed only by workers wearing rubber gloves. They are highly stable; in resistance to aerial oxidation and in constancy of results when used repeatedly they are far superior to the highly alkaline baths of the prior art, and compare favorably with the best conventional separate developing and fixing formulas. They also compare well with these conventional separate formulas in useful life, as measured by the area of photographic material that can be processed in a given volume of solution before the bath ceases to give acceptable results.

These new baths have the further advantage that they can be employed with satisfactory results over a much wider range of temperatures than either conventional separate developing and fixing baths or the combined developing and fixing baths of the prior art. The highly alkaline prior art baths cited cause reticulation and frilling of the gelatine layers of plates and films if used at temperatures higher than about 75 degrees F., whereas the baths disclosed in the Goldhammer and Maurer application may be used at temperatures as high as 85 degrees F. with normal plates and films and at higher temperatures with pre-hardened emulsions. When used over a wide range of temperature the new baths produce much more nearly constant results, in terms of density and contrast of the images, than conventional separate developing and fixing baths. It is well known that in an ordinary developer the rate of development increases with rising temperature. In the combined developing and fixing bath the same increase of the rate of development occurs, but the final extent of development is limited because the rate of fixation is also increased at higher temperatures. The net effect is that over the range from 60 degrees to 85 degrees F. the variation of gamma and density of the image is no greater than occurs with conventional developers over the range from 65 to 75 degrees.

My present invention is an improvement on the invention of Goldhammer and Maurer in that it provides combined developing and fixing baths of still higher activity, better stability, and longer useful life. At the same time it provides baths which produce images of exceptionally fine grain and enhanced resolution of fine details. This is accomplished without the loss of effective emulsion speed which in the past has generally been one of the results of extremely fine-grain developing procedures. Baths made up in accordance with the invention of Goldhammer and Maurer and incorporating my present invention also produce lower chemical fog than other combined developing and fixing compositions adjusted to produce comparable densities and gammas.

These and other desirable results which will be apparent from this disclosure are obtained by properly compounding a bath containing amidol and one or more of the dihydroxy-benzenes, as disclosed by Goldhammer and Maurer, in combination with an alkali metal hydroxide as the alkali and ammonium thiosulfate as the fixing agent, with appropriate additions of another developing agent of the density building, low fogging type, an anti-foggant, and an inorganic reducing agent such as sodium sulfite.

In previously described combined developing and fixing baths sodium thiosulfate has been employed as the fixing agent. Substitution of ammonium thiosulfate for sodium thiosulfate in these prior art compositions is not practical because the fixing action of ammonium thiosulfate is too rapid.

In compounding a bath for combined developing and fixing it is necessary to adjust the amount of fixing agent so that the fixing rate is in the proper relation to the rate at which the most energetic developing agent present is able to initiate development of the latent image cen-

ters. If fixation proceeds to any appreciable extent before development of these latent image centers has begun, many of them are destroyed, and when this occurs there is serious loss of speed of the photographic emulsion being processed. Furthermore, a too rapid fixing action reduces the contrast of the images even when the exposure has been increased to compensate for the loss of effective emulsion speed, so that negatives produced in a bath in which this condition exists do not have the characteristics that are desirable for printing.

In the formulas of the prior art, almost without exception, the most energetic developing agent has been monoethyl para-aminophenol sulfate, commonly known as metol. With this agent, in order to secure a rapid enough initiation of development of the latent image centers to avoid substantial loss of film speed, it is necessary either to raise the alkalinity of the bath to a pH of 11.0 or higher or to carry out the processing at a temperature substantially higher than the commonly accepted optimum temperature of 68 degrees F. The rate of development so obtained is in proper relation to the rate of fixing by sodium thiosulfate. If an attempt is made to substitute ammonium thiosulfate as the fixing agent in such a bath we find that there is serious loss of effective emulsion speed and contrast unless the amount of ammonium thiosulfate is reduced to such a point that it is exhausted in the fixation of the first few films or plates processed. In this case the bath is necessarily unstable and has an extremely short life.

In contradistinction to these disadvantages which make ammonium thiosulfate unsuitable for use as the fixing agent in baths compounded according to the teachings of the prior art, I have found that ammonium thiosulfate in combination with an alkali metal hydroxide (usually sodium hydroxide) is well suited for use in baths containing amidol and one or more of the dihydroxybenzenes, as disclosed in the application of Goldhammer and Maurer, and in such baths this combination is highly advantageous in several ways.

In the application of Goldhammer and Maurer it is disclosed that amidol, which by itself has poor keeping quality even in neutral or slightly acid solutions of sodium sulfite, and which has extremely short active life in alkaline solutions, is preserved to a remarkable degree in the presence of any of the three dihydroxybenzenes. As disclosed in the table of the above identified application, the dihydroxybenzene to developing agent ratio is in the range from 7.5% to 200% by weight. This preservative action of hydroquinone, pyrocatechol, or resorcinol (or any combination of them) makes it practical to employ amidol in alkaline solution as the agent to initiate development. When so used it acts so rapidly that in combined developing and fixing baths it becomes practical to employ a fixing agent as rapid as ammonium thiosulfate.

In order to fix a given area of photographic emulsion only about half as much ammonium thiosulfate is needed as is needed of the more commonly used sodium thiosulfate. This smaller quantity nevertheless produces complete fixation in a shorter time than sodium thiosulfate. Taken together, these characteristics of ammonium thiosulfate make it possible to accomplish a major reduction of the total salt content of the bath. This results in higher developing activity, other factors being equal. The reduction in total salt content can be accomplished to the greatest degree when an alkali metal hydroxide such as sodium hydroxide is used in combination with the ammonium thiosulfate.

The combination of ammonium thiosulfate and an alkali metal hydroxide is particularly advantageous also because of the fact that ammonium thiosulfate is an acid salt. This property enables the thiosulfate to act as a buffer, reducing and stabilizing the alkalinity produced by a given amount of the hydroxide in such a way that it is easy to obtain a stable bath of the requisite pH. This result is not obtainable by combining an alkali metal hydroxide with a substantially neutral fixing agent such as sodium thiosulfate; nor is it obtained by combining a less powerful alkali such as sodium carbonate with ammonium thiosulfate.

In the first of these cases we find that the quantity of sodium hydroxide needed to give a pH of 8.0 to 9.5 in a bath with sodium thiosulfate is so small that aerial oxidation causes rapid loss of developing activity. This occurs because the sodium hydroxide takes part in the chemical reaction by which the developing agents are oxidized. When the hydroxide is present in only small quantities, the aerial oxidation of small quantities of the developing agents present can in this way remove enough of the alkali to cause a substantial reduction of the pH of the bath, and since the developing activity depends on the maintenance of a suitable pH value, the activity of the bath falls much more rapidly than the concentration of the relatively costly developing agents.

In the second case we find that because of the acid character of ammonium thiosulfate it is necessary to add large quantities of a milder alkali such as sodium carbonate to obtain even moderate pH values such as 8.0 to 9.0 in a bath where this fixing agent is used. This defeats the objective of obtaining a bath of low total salt content and even leads to formulas in which the content of sodium carbonate is so near the point of saturation that a moderate drop in temperature causes this component to precipitate out of the bath.

Because of the buffering action of the ammonium thiosulfate I have found that it is feasible to use, in combination with it, an amount of sodium hydroxide or other alkali metal hydroxide large enough to make the quantity removed by the aerial oxidation reaction of negligible importance, while at the same time the desired pH in the range from 8.0 to 9.5 is obtained and the total salt content of the bath is held to a desirably low value.

As an example of the improvement obtained in this respect, we may compare Keelan's Formula No. 315, to which reference has already been made, with a formula of somewhat greater activity prepared in accordance with the present invention. The prior art formula has a total salt content of 305 grams per liter, of which 35 grams are sodium hydroxide, giving a pH of 11.55. 110 grams of the total of 305 are sodium thiosulfate. This prior art formula requires brush agitation, which is in effect equivalent to a ⅓ increase in time (as reported on page 524, Table LVIII of "The Theory of the Photographic Process" by C. E. Kenneth Mees) to process rapid panchromatic film in 3 minutes at 75 degrees F. The formula prepared in accordance with the present invention, which is the first of several examples to be given later, has a total salt content of 120 grams per liter, of which 20 grams are sodium hydroxide, giving a pH of 8.7 in the presence of 50 grams of ammonium thiosulfate. This formula gives the same gamma and image density as the Keelan formula in 3 minutes at 68 degrees F. without agitation. It may further be noted that the prior art formula contains 50 grams of developing agents per liter whereas the formula in accordance with the present invention contains only 30 grams of developing agents per liter. This is a further indication of the degree to which a high total salt content depresses developing activity.

A further comparison which shows the improvement effected by my invention in reducing the salt content of the combined developing and fixing bath and thereby providing a bath of greater activity is the comparison between the first formula given by way of example in the Goldhammer and Maurer application and the first example in the present application. The referenced formula in the Goldhammer and Maurer application employs sodium thiosulfate as the fixing agent and sodium carbonate as the alkali. It contains a total of 30 grams of developing agents per liter, and has a total salt content of 200 grams per liter. The pH is 9.5. This bath gives a gamma

of 0.75 on fast films in a processing time of 6 minutes at 68 degrees F. The bath prepared in accordance with the present invention, using ammonium thiosulfate in combination with sodium hydroxide and having the same quantities of the same developing agents, has a salt content of 120 grams per liter and a pH of 8.7, as before stated, and gives, with the same film, a gamma of 0.85 in a processing time of 3 minutes at 68 degrees F. Since the two baths differ only in the combinations of chemicals used as alkali and fixing agent and in the resulting salt content and pH, the comparative results show how strongly reduction of salt content favors higher activity, since the bath prepared in accordance with the present invention gives a higher gamma in a shorter time and at a lower value of pH.

It is a further advantage of baths compounded in accordance with the present invention that the grain of the images produced is finer than is obtained with any previously described combined developer and fixer of comparable activity. Heretofore high activity has been obtained by higher alkalinity, a condition conducive to clumping of the silver particles. The much lower alkalinity of the present baths favors finer grain, and this tendency is aided by the strong silver halide solvent action of the ammonium thiosulfate.

Amidol has the characteristic action of first forming an image of low contrast with extreme rapidity and then building contrast and density much more slowly. By proper selection of the relative concentrations of the amidol and the ammonium thiosulfate and proper adjustment of the alkalinity, I obtain a bath in which development of the latent image centers is begun within a small fraction of a second, and therefore with minimum loss of effective emulsion speed, while grain clumping does not occur because fixation is complete before this stage in the action of the amidol can be reached. This proper proportioning of the concentrations of the amidol and the ammonium thiosulfate also minimizes chemical fog, which would reach high values if the action of the amidol were prolonged.

The low contrast image obtained in the first few seconds of processing by the action of the amidol contains substantially all the detail that has been impressed on the photographic emulsion by the exposure it has received. This image can be given greatly increased contrast and density by adding to the bath, as before stated, a developing agent such as chlorohydroquinone, dichlorohydroquinone, bromohydroquinone, dibromohydroquinone, para-hydroxyphenyl glycin, or any other organic developing agent having similar properties. All of these agents may properly be described as rapid density-building, low fogging agents. They lack the ability possesed by amidol (and to a lesser extent by metol) of initiating development with extreme rapidity, but once development has begun they carry it forward more rapidly than the powerful initiating agents. Of the density-building agents listed, para-hydroxyphenyl glycin, commonly called simply glycin, is preferred where minimum grain size of the developed image is of importance.

Pyrocatechol, one of the dihydroxybenzenes, has properties such that it may be used as an effective density building, low fogging agent. The amount required to perform this function is considerably in excess of the amount that is required when pyrocatechol is used primarily as a preservative of the amidol. As an amidol preservative a weight of pyrocatechol equal to between 20 percent and 40 percent of the weight of the amidol is sufficient. When the pyrocatechol is to serve also as the density building agent the quantity should be increased to between 75 and 150 percent of the weight of the amidol. A specimen formula of this type, containing amidol and pyrocatechol as the only developing agents, is given among the examples which follow.

The use of an auxiliary density building developing agent such as any of those listed is of particular advantage when baths are compounded in accordance with my invention because with these baths fixation is completed in comparatively short times, and therefore it is essential that the developing agents build density and contrast quickly.

The concentrations of the ingredients of combined developing and fixing baths utilizing my present invention may be varied in the generally known manner within wide limits in order to produce gammas ranging from as low as 0.3 to as high as 1.4 in order to suit the intended application. As in conventional processing the inherent characteristics of the photographic film or plate partially determine the gamma obtained with any formula. The following formulas are typical of those I have found to be suitable for various applications.

No. 1.—Application—processing of high and medium speed panchromatic and orthochromatic roll films:

Water (120° F.)	cc	750
Sodium Sulfite (anhydrous)	g	50
Amidol	g	15
Hydroquinone	g	5
Glycin	g	10
6-nitrobenzimidazole nitrate, 0.5 percent solution	cc	80
or		
Potassium bromide	g	5
Sodium hydroxide	g	20
Ammonium Thiosulfate	g	50

Water to make 1000 cc.

pH=8.7. Time, 3 minutes at 68° F. Gamma on high speed panchromatic films, 0.85.

No. 2.—A formula using pyrocatechol, for the same application as No. 1:

Water (120° F.)	cc	750
Sodium Sulfite (anhydrous)	g	50
Amidol	g	15
Pyrocatechol	g	15
Potassium bromide	g	5
Sodium hydroxide	g	25
Ammonium thiosulfate	g	50

Water to make 1000 cc.

pH=9.3. Time, 3 minutes at 68° F. Gamma on high speed panchromatic films 0.85.

No. 3.—Application—processing of high speed panchromatic motion picture negative films:

Water (120° F.)	cc	750
Sodium Sulfite (anhydrous)	g	32
Amidol	g	10
Hydroquinone	g	3.2
Glycin	g	6.4
6-Nitrobenzimidazole nitrate, 0.5 percent solution	cc	40
or		
Potassium bromide	g	2.5
Sodium hydroxide	g	10
Ammonium thiosulfate	g	56

Water to make 1000 cc.

pH=8.5. Time, 3 minutes at 68° F. Gamma 0.60 on panchromatic negative motion picture film.

No. 4.—A formula using only amidol and hydroquinone, suitable for panchromatic motion picture negative films:

Water (120° F.)	cc	750
Sodium sulfite (anhydrous)	g	40
Amidol	g	15
Hydroquinone	g	5
6-nitrobenzimidazole nitrate	g	0.4

Sodium hydroxide	g..	10
Ammonium thiosulfate	g..	50

Water to make 1000 cc.

pH=9.0. Time, 3 minutes at 68° F. Gamma 0.65.

No. 5.—A formula for applications requiring higher contrast:

Water (120° F.)	cc..	750
Sodium sulfite	g..	30
Amidol	g..	15
Hydroquinone	g..	5
Glycin	g..	10
6-nitrobenzimidazole nitrate 0.5 percent solution	ml..	80
Sodium hydroxide	g..	15
Ammonium thiosulfate	g..	25

Water to make 1000 cc.

pH=9.5. Time, 6 minutes at 68° F. Gamma on high speed panchromatic films 1.0, on medium speed panchromatic films 1.2 to 1.4.

I have found that the ingredients of any of the above formulas, with the exception of the water, may be mixed together in dry form in the proportions stated, and that these mixtures have excellent keeping qualities as long as they are kept in airtight containers. Combined developing and fixing baths can then be prepared conveniently as needed by dissolving one of these mixtures of dry chemicals in the appropriate volume of water.

What is claimed is:

1. In a chemical composition of increased activity and having in aqueous solution a pH value not in excess of 9.5 and adapted for combined developing and fixing of silver halide photographic emulsions, containing a developing agent selected from the group consisting of 2,4 diaminophenol, 2,4 diaminoresorcinol, 6-methyl 2,4, diamino-phenol, 5-methyl 2,4 diaminophenol, 4-amino-6 - methyl - 2 - methyl - amino - phenol, 6 - amino - 4-methyl-2-methylamino-phenol, 5 dimethylamino-2-methyl-amino-phenol, 1,2,4, triamino-benzene, 5-methyl 1,2,4 triamino benzene, 4 hydroxy : 2'4' diaminodiphenylamine, 4 : 2'4' triaminodiphenylamine, and 1,3 diamino 4,6 dihydroxybenzene; and a dihydroxybenzene selected from the group consisting of pyrocatechol, resorcinol and hydroquinone; the ratio of the dihydroxybenzene to the developing agent being in the range from 7.5% to 200% by weight, the combination of an alkali metal hydroxide and ammonium thiosulfate.

2. In a chemical composition of increased activity and having in aqueous solution a pH value not in excess of 9.5 and adapted for combined developing and fixing of silver halide photographic emulsions, containing a developing agent selected from the group consisting of 2,4 diaminophenol, 2,4 diaminoresorcinol, 6-methyl 2,4, diamino-phenol, 5-methyl 2,4 diaminophenol, 4-amino-6 - methyl - 2 - methyl - amino - phenol, 6 - amino - 4 - methyl - 2 - methylamino-phenol, 5 - dimethylamino - 2-methyl-amino-phenol, 1,2,4, triamino-benzene, 5-methyl 1,2,4 triamino benzene, 4 hydroxy : 2'4' diaminodiphenylamine, 4 : 2'4' triaminodiphenylamine, and 1,3 diamino 4,6 dihydroxybenzene; and a dihydroxybenzene selected from the group consisting of pyrocatechol, resorcinol and hydroquinone; the ratio of the dihydroxybenzene to the developing agent being in the range from 7.5% to 200% by weight, the combination of sodium hydroxide and ammonium thiosulfate.

3. In a chemical composition of increased activity and having in aqueous solution a pH value not in excess of 9.5 and adapted for combined developing and fixing of silver halide photographic emulsions, containing amidol and a dihydroxybenzene selected from the group consisting of pyrocatechol, resorcinol and hydroquinone; the ratio of the dihydroxybenzene to the amidol being in the range

from 7.5% to 200% by weight, the combination of sodium hydroxide and ammonium thiosulfate.

4. In a chemical composition of increased activity and having in aqueous solution a pH value not in excess of 9.5 and adapted for combined developing and fixing of silver halide photographic emulsions, containing amidol and hydroquinone, the hydroquinone to amidol ratio being in the range from 7.5% to 200% by weight, the combination of sodium hydroxide and ammonium thiosulfate.

5. An aqueous solution having a pH value not in excess of 9.5 and adapted for the combined development and fixing of silver halide photographic emulsions containing the ingredients listed in the following formula in substantially the relative proportions stated:

Water	liter..	1
Anhydrous sodium sulfite	grams..	50
Amidol	do....	15
Hydroquinone	do....	5
Glycin	do....	10
6 - nitrobenzimidazole nitrate (0.5 percent solution)	cc..	80
Sodium hydroxide	grams..	20
Ammonium thiosulfate	do....	50

6. A dry mixture adapted to be dissolved in water to produce a solution having a pH value not in excess of 9.5 and for the combined developing and fixing of silver halide photographic emulsions, containing the following ingredients in substantially the proportions stated:

	Parts by weight
Anhydrous sodium sulfite	50
Amidol	15
Hydroquinone	5
Glycin	10
6-nitrobenzimidazole nitrate	0.4
Sodium hydroxide	20
Ammonium thiosulfate	50

7. An aqueous solution according to claim 4 containing the ingredients listed in the following formula in substantially the relative proportions stated:

Water	liter..	1
Anhydrous sodium sulfite	grams..	50
Amidol	do....	15
Hydroquinone	do....	5
Glycin	do....	10
Potassium bromide	do....	5
Sodium hydroxide	do....	20
Ammonium thiosulfate	do....	50

8. A dry mixture adapted to be dissolved in water to produce a solution according to claim 4, containing the following ingredients in substantially the proportions stated:

	Parts by weight
Anhydrous sodium sulfite	50
Amidol	15
Hydroquinone	5
Glycin	10
Potassium bromide	5
Sodium hydroxide	20
Ammonium thiosulfate	50

9. An aqueous solution according to claim 4 containing the ingredients listed in the following formula in substantially the relative proportions stated:

Water	liter..	1
Sodium sulfite (anhydrous)	grams..	32
Amidol	do....	10
Hydroquinone	do....	3.2
Glycin	do....	6.4
6 - nitrobenzimidazole nitrate (0.5 percent solution)	cc..	40
Sodium hydroxide	grams..	10
Ammonium thiosulfate	do....	56

10. A dry mixture adapted to be dissolved in water to produce a solution according to claim 4, containing the following ingredients in substantially the proportions stated:

	Parts by weight
Sodium sulfite (anhydrous)	32
Amidol	10
Hydroquinone	3.2
Glycin	6.4
6-nitrobenzimidazole nitrate	0.2
Sodium hydroxide	10
Ammonium thiosulfate	56

11. An aqueous solution according to claim 4 containing the ingredients listed in the following formula in substantially the relative proportions stated:

Water	liter	1
Sodium sulfite (anhydrous)	grams	40
Amidol	do	15
Hydroquinone	do	5
6-nitrobenzimidazole nitrate	do	0.4
Sodium hydroxide	do	10
Ammonium thiosulate	do	50

12. A dry mixture adapted to be dissolved in water to produce a solution according to claim 4, containing the following ingredients in substantially the proportions stated:

	Parts by weight
Sodium sulfite (anhydrous)	40
Amidol	15
Hydroquinone	5
6-nitrobenzimidazole nitrate	0.4
Sodium hydroxide	10
Ammonium thiosulfate	50

13. An aqueous solution according to claim 4 containing the ingredients listed in the following formula in substantially the relative proportions stated:

Water	liter	1
Sodium sulfite (anhydrous)	grams	30
Amidol	do	15
Hydroquinone	do	5
Glycin	do	10
6-nitrobenzimidazole nitrate (0.5% solution)	cc	80
Sodium hydroxide	grams	15
Ammonium thiosulfate	do	25

14. A dry mixture adapted to be dissolved in water to produce a solution according to claim 4, containing the following ingredients in substantially the proportions stated:

	Parts by weight
Sodium sulfite (anhydrous)	30
Amidol	15
Hydroquinone	5
Glycin	10
6-nitrobenzimidazole nitrate	0.4
Sodium hydroxide	15
Ammonium thiosulfate	25

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