

RESERVE COPY

PATENT SPECIFICATION



Application Date: Sept. 7, 1935. No. 24975/35.

462,140

Complete Specification Left: Aug. 18, 1936.

Complete Specification Accepted: March 3, 1937.

PROVISIONAL SPECIFICATION

Improvements in Photographic Developing Solutions for Colour Photography

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, and EDWIN ERNEST JELLEY, a British Subject, of Kodak Works, Wealdstone, Middlesex, England, do hereby declare the nature of this invention to be as follows:—

This invention relates to photographic developing solutions and more particularly to developing solutions comprising colour forming compounds, known as colour developers.

Colour developers usually contain two components which under a suitable oxidising action, such as that produced by reaction with exposed silver halides in photographic emulsions, will couple together to produce a dyestuff. In almost all cases, however, the oxygen of the air is sufficient to produce coupling and for this reason it is usual to include in such developers substantial quantities of sodium sulphite which itself can absorb oxygen and has a well-known preserving action on photographic developers. Although sodium sulphite is very satisfactory in the case of almost all ordinary so-called black and white developers, it is not entirely satisfactory in the case of colour developers. These latter, even shortly after they are compounded, often give coloured solutions, despite the presence of sodium sulphite due apparently to the inability of the sodium sulphite to prevent entirely the coupling taking place prematurely in the solution.

This invention is based on the discovery that there are oxidisable substances which, although when used in place of or in addition to sodium sulphite in ordinary black and white developers yield no particular advantage, do yield a most surprising advantage in the case of colour developers in overcoming the very undesirable tendency of the colour components to couple under the action of atmospheric oxygen, at least in all but the most difficult cases, e.g. *p*-nitrophenacetone. The substances which we find give this surprising result are a formaldehyde sulphoxylate, e.g. the sodium salt; hydrazine compounds and hydroxylamine compounds, e.g. their hydrates. These

substances have a greater reducing power than sodium sulphite but a less reducing power than sodium hydrosulphite. It is essential to use a reducing agent which does not decolour the wanted dyestuff formed in the photographic image. Formaldehyde sulphoxylates are preferable because hydrazine and hydroxylamine have a tendency to produce blisters in the gelatine due to the formation of small bubbles of nitrogen.

Colour developers which may be made up according to the present invention are described in the following examples.

EXAMPLE 1.

A colour developer for blue-green is made up by mixing together equal parts of the two following solutions:

(a) <i>p</i> -aminodiethylaniline			
monohydrochloride	-	3	grams.
sodium formaldehyde			
sulphoxylate	-	5	”
sodium carbonate	-	50	”
potassium thiocyanate	-	0.5	”
water to	-	1000	ccs.
(b) <i>o</i> -hydroxyl-diphenyl	-	2.5	grams.
methyl alcohol	-	100	ccs.

With couplers giving yellow and blue dyes we find that our invention is very valuable. Although sodium formaldehyde sulphoxylate does not eliminate the tendency to couple in the solution in the case of red developers containing *p*-nitrophenacetone, which appears to be particularly reactive, the present invention has enabled us to compound a satisfactory colour developer for red as shown in the following example:—

EXAMPLE 2.

(a) Diethyl - <i>p</i> - phenylene-			
diamine hydrochloride	-	2	grams.
sodium formaldehyde			
sulphoxylate	-	5	”
2 N ammonia solution	-	80	ccs.
Water to make	-	1000	ccs.
(b) β -naphthoyl acetone			
nitrile	-	5	grams.
2 N sodium hydroxide			
solution	-	20	ccs.
isopropyl alcohol	to		
make	-	200	ccs.

To produce a red colour developer mix one part of solution (b) to eight parts of solution (a).

It will be noted that the solutions in Example 2 do not contain any sodium carbonate or sodium sulphite. The alkali is in the form of sodium ion hydroxide which enables the concentration of the sodium to be kept low where-
 5 by difficulties arising through salting out are avoided. This feature can be utilised in the production of colour developers for
 10 blue and yellow as in the following examples:—

EXAMPLE 3.

o-phenyl-phenol - - - 4 grams.
 2 N sodium hydroxide
 15 solution - - - 20 ccs.
 Water to make - - - 200 ccs.

EXAMPLE 4.

acetoacet - 2:5 - dichlor-
 anilide - - - 5 grams.
 20 2 N sodium hydroxide
 solution - - - 20 ccs.
 isopropyl alcohol - - 100 ccs.
 Water to make - - - 200 ccs.
 To produce a colour developer for blue

mix one part of the solution of Example 25
 3 and 10 parts of solution (a) of Example 2.

To produce a colour developer for yellow mix one part of the solution of Example 4 and eight parts of solution (a)
 30 of Example 2.

It will be noted that very conveniently the solution (a) of Example 2 is common for compounding developers for red, blue and yellow according to Examples 2, 3
 35 and 4.

Substances such as hydrazine which are nuclear forming substances for silver halide emulsions (see Patent No. 341,183) have the added advantage, e.g. in reversal
 40 processes, of obviating the exposure to light which would otherwise be necessary before the second development.

Dated this 7th day of September, 1935.

W. P. THOMPSON & CO.,

Chartered Patent Agents,

12, Church Street, Liverpool, 1.

COMPLETE SPECIFICATION

Improvements in Photographic Developing Solutions for
 Colour Photography

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, and EDWIN ERNEST JELLEY, a British Subject, of Kodak Works, Wealdstone, Middlesex, England, do hereby declare the nature of this invention and in what manner the same is
 50 to be performed. to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in colour forming developers.

It is known that coloured photographic images may be formed by using a developer which forms a coloured compound on development. The coloured compound thus formed is deposited adjacent to the silver grains of the silver image during development. It is also known that a coloured image may be formed by effecting the development in presence of a compound, termed a colour coupler, which couples during development with the oxidation product of the developing agent and forms a colouring substance which is likewise deposited adjacent to the silver grains of the silver image during development. In either of these cases the coloured compound is formed by a coupling reaction following the oxidation of the developing agent by the silver salt undergoing development.

In almost all cases, however, the oxygen of the air is sufficient to give rise to the coupling reaction and for this reason it is usual to include in such developers sub-

stantial quantities of sodium sulphite
 80 which itself can absorb oxygen and has a well-known preserving action on photographic developing agents. Although sodium sulphite is very satisfactory in the case of almost all ordinary so-called black
 85 and white developers, it is not entirely satisfactory in the case of colour developers, possibly due to the high proportion of alkali required in such colour developers. Colour developers which
 90 form coloured compounds on development or which contain a developing agent and a colour coupler, often give coloured solutions, even shortly after they are compounded, despite the presence of
 95 sodium sulphite and as the oxygen of the air penetrates into the solution more and more dye is produced and the colour deepens.

This invention is based on the discovery
 100 that there are oxidisable substances which, although when used in place of or in addition to sodium sulphite in ordinary black and white developers yield no particular advantage, do yield a most sur-
 105 prising advantage in the case of colour developers in overcoming the very undesirable tendency towards coupling under the action of atmospheric oxygen of the air, at least in all but the most diffi-
 110 cult cases, e.g. *p*-nitrophenacetone. The substances which we find give this surprising result are a formaldehyde sulphoxylate, e.g. the sodium salt; a hydrazine or a hydroxylamine. By the
 115

- expressions "a hydrazine" and "a hydroxylamine" we mean these bases themselves or their hydrates or their homologues and the hydrates of these.
- 5 These substances possess the common property that they have a greater reducing power than sodium sulphite but a less reducing power than sodium hydro-sulphite.
- 10 It is essential to use a reducing agent which does not decolour the wanted dye-stuff formed in the photographic image. Formaldehyde sulphonylates are preferable because hydrazine and hydroxylamine
- 15 have a tendency to produce blisters in the gelatine due to the formation of small bubbles of nitrogen.
- The colour developers of the present invention preferably contain an aromatic
- 20 amino developing agent and a colour coupler.
- Colour developers which may be made up according to the present invention are described in the following examples.
- 25 **EXAMPLE 1.**
A colour developer for blue-green is made up by mixing together equal parts of the two following solutions:
- 30 (a) *p*-aminodiethylaniline monohydrochloride - 3 grams.
sodium formaldehyde sulphonylate - 5 "
sodium carbonate - 50 "
35 potassium thiocyanate - 0.5 "
water to - - - 1000 ccs.
- (b) *o*-hydroxyl-diphenyl - 2.5 grams.
methyl alcohol - 100 ccs.
- 40 With couplers giving yellow and blue dyes we find that our invention is very valuable. Although sodium formaldehyde sulphonylate does not eliminate the tendency to couple in the solution in the case of red developers containing *p*-nitrophenacetonitrile, which appears to be particularly reactive, the present invention has enabled us to compound a
- 45 satisfactory colour developer for red as shown in the following example:—
- 50 **EXAMPLE 2.**
(a) Diethyl - *p*-phenylene-diamine hydrochloride 2 grams.
sodium formaldehyde sulphonylate - 5 "
55 2 N ammonia solution 80 ccs.
Water to make - 1000 ccs.
- (b) β -naphthoyl acetonitrile 5 grams.
2 N sodium hydroxide solution - 20 ccs.
- 60 isopropyl alcohol to make - - - 200 ccs.
- To produce a red colour developer mix one part of solution (b) to eight parts of solution (a).
- 65 It will be noted that the solutions in Example 2 do not contain any sodium carbonate or sodium sulphite. The alkali is in the form of sodium hydroxide which enables the concentration of the sodium to be kept low where-
by difficulties arising through salting out are avoided. This feature can be utilised in the production of colour developers for blue and yellow as in the following examples:—
- 70 **EXAMPLE 3.**
o-phenyl-phenol - 4 grams.
2 N sodium hydroxide solution - 20 ccs.
Water to make - 200 ccs.
- 75 **EXAMPLE 4.**
acetoacet - 2:5 - dichloro-anilide - 5 grams.
2 N sodium hydroxide solution - 20 ccs.
80 isopropyl alcohol - 100 ccs.
Water to make - 200 ccs.
- To produce a colour developer for blue mix one part of the solution of Example 3 and 10 parts of solution (a) of Example 2.
- 85 To produce a colour developer for yellow mix one part of the solution of Example 4 and eight parts of solution (a) of Example 2.
- 90 It will be noted that very conveniently the solution (a) of Example 2 is common for compounding developers for red, blue and yellow according to Examples 2, 3 and 4.
- 95 Substances such as hydrazine which are nuclear forming substances for silver halide emulsions (see Patent No. 341,183) have the added advantage, e.g. in reversal processes, of obviating the exposure to light which would otherwise be necessary before the second development.
- 100 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—
- 105 1. A colour developer comprising a developing agent for silver salt the oxidation product of which gives rise to a dyestuff, by coupling, along with the silver which is being produced by development and containing, as preservative, a formaldehyde sulphonylate, a hydrazine or a hydroxylamine.
- 110 2. A colour developer comprising a developing agent for silver salt, a colour coupler which couples with the oxidation product of the developing agent to produce a dyestuff along with the silver which is being produced by development, and a preservative in which the preservative is a formaldehyde sulphonylate, a hydrazine or a hydroxylamine.
- 115 3. A colour developer as claimed in 130

Claim 2 in which the developing agent is amino developing agent.

4. A colour developer as claimed in any of the preceding claims containing 5 alkali substantially entirely in the form of caustic alkali.

5. A developer for use in conjunction with a colour coupler containing an aromatic amino developing agent and as 10 preservatives a formaldehyde sulphoxylate

or a hydrazine, or a hydroxylamine.

6. The developing solutions for colour development containing as preservative, formaldehyde sulphoxylate, substantially as described in each of the foregoing 15 examples.

Dated this 17th day of August, 1936.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1937.