

AMENDED SPECIFICATION

Reprinted as amended under Section 8 of the Patents and Designs Acts, 1907 to 1932.

PATENT SPECIFICATION

Application Date: April 23, 1936. No. 11551/36.

478,942

Complete Specification Left: April 23, 1937.

Accepted: Jan. 24, 1938.



PROVISIONAL SPECIFICATION

Improvements in and relating to Colour Forming Developers and Processes of Colour Development

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to improvements in colour forming developers and in processes of colour development for use in connection with colour photography.

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 the development. It is also known that a coloured image may be formed by adding to certain developer solutions a compound 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. Such a compound, which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product thereof during development, is referred to herein as a colour coupler.

The present invention concerns new or improved colour forming developers comprising an aromatic amino compound serving as the developing agent and a colour coupler as hereinafter defined and also includes a new or improved colour development process which consists in developing a reducible silver salt image in a photographic element with the aid of an aromatic amino compound in presence of a colour coupler as hereinafter defined.

The silver can be removed from the image after colour development leaving a clear transparent dye image.

The invention also includes a photographic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling *in situ* during development of a colour coupler as hereinafter defined with the oxidation product of an aromatic amino developing agent.

When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour couplers during development to form dyes. If such colour couplers are added to the developer solution, or incorporated in the emulsion layer, the dye which is thus formed by coupling during development is deposited in the gelatine or other silver halide carrier adjacent to the metallic silver grain. It is desirable that the dyes thus formed should not readily wander from the place of formation. It is accordingly, desirable that they should be insoluble in water. They are not physically attached to the silver grain and therefore the silver may be subsequently bleached out of the carrier layer leaving a pure dye image.

Numerous substances have hitherto been employed or proposed as colour couplers among which may be mentioned phenols, naphthols, cresols, nitrophenylacetone, nitrile and acetoacetic esters. It has not, however, always been possible among those hitherto available to select one which exhibits all the desired combination of properties required for any specific case. In colour-developing a gelatino-silver halide emulsion layer it is neces-

{Price 1/-}

Price 4s 6d

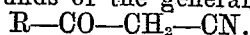
sary to select a colour coupler which will give just the desired shade in conjunction with the colours which are produced in other layers. It is moreover important to

5 employ a colour coupler which gives a coloured compound which is resistant to the normal processing baths employed, although it may often be desirable to have one which gives a colour which can be

10 destroyed and/or removed if desired during some step in the processing. Many of the colour couplers employed according to the present invention are suitable in carrying out the processing described

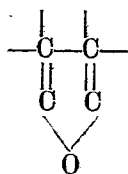
15 in our prior Patents Nos. 427,472, 427,516, 427,518, 427,520, 440,032, 440,089, and Application No. 16012/35.

According to the present invention the substances employed as colour couplers are compounds of the general formula



R = a substituted benzene nucleus including phenyl and phenol substituents or fused on rings but excluding a trimethyl substituted phenyl group.

The invention also includes compounds having a reactive methylene group and containing the grouping



- 30 *p*-Phenylbenzoylacetonitrile
p-(*p*¹-Chlorophenyl)benzoylacetonitrile
p-Phenoxybenzoylacetonitrile
 α -Naphthoylacetonitrile
 35 2-Methyl- α -naphthoylacetonitrile
 4-Methyl- α -naphthoylacetonitrile
 2-Methoxy- α -naphthoylacetonitrile
 4-Methoxy- α -naphthoylacetonitrile
 β -Naphthoylacetonitrile
 1-Methyl-2-naphthoylacetonitrile
 40 6-Methyl-2-naphthoylacetonitrile
 7-Methyl-2-naphthoylacetonitrile
 1-Methoxy-2-naphthoylacetonitrile
 Tetrahydro- β -naphthoylacetonitrile
 3- ω -Cyanoacetylnaphthene
 45 3- ω -Cyanoacetyldiphenyleneoxide
 2-(ω -Cyanoacetyl)-coumarone

The colours given by the colour couplers named above when used in conjunction with *p*-aminodiethylaniline, for example, as developing agent are red to magenta. 50

The aromatic amino compounds which may be used as developing agents in the present invention include the mono-di-, and tri-amino aryl compounds. Among the monoamino compounds may be mentioned the aminophenols, aminocresols and their halogen substituted derivatives as well as the aminonaphthols. The developing agents usually used are the diamino compounds such as para-phenylene diamine and its substitution products. These developing agents may be substituted in the amino groups or in the ring or in both, forming compounds such as the alkyl phenylene diamines, toluylene-diamines, alkyl-toluylene diamines and aminodiphenylamines. These compounds are usually kept in the salt form such as hydrochloride or sulphate since these are more stable than the amines themselves. 55

As examples of developing agents of this class, there may be mentioned diethyl para-phenylene diamine, mono-methyl paraphenylene diamine, dimethyl paraphenylene diamine and ortho-amino-diethyl-aniline. 60

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The present invention may be utilised in the formation of coloured photographic images on plates or paper as well as on films and the dyes will be formed when gelatine or other carrier for the silver halide is used. The plates, films or papers may have differently sensitized emulsions of the mixed grain type or superimposed on one side or on both sides of the support. The dyes formed may be decolourized by an oxidizing agent such as chromic acid and colourless soluble compounds thereby formed. The bleaching of the dye in this manner need not destroy the silver image but may convert it into a developable silver salt image which can in turn be coloured, bleached and recoloured a number of times. 80

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Dated this 22nd day of April, 1936.
 W. P. THOMPSON & CO.,
 12, Church Street, Liverpool, 1,
 Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in and relating to Colour Forming Developers and Processes of Colour Development

95 We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this inven-

tion which has been communicated to us by Eastman Kodak Company, a Company 100 organised under the Laws of the State of New Jersey, United States of America, of

343, State Street, Rochester, New York, United States of America, and in what manner the same is to be performed, to be particularly described and ascertained

5 in and by the following statement:—

This invention relates to improvements in colour forming developers and in processes of colour development for use in connection with colour photography.

10 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 the development. It is also known that a coloured image may be formed by adding to certain developer solutions or by incorporating in the gelatino-silver halide emulsion before or after exposure a compound 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. Such a compound, which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product thereof during development, is referred to herein as a colour coupler.

The present invention concerns new or improved colour forming developers comprising an aromatic amino compound serving as the developing agent and a colour coupler as hereinafter defined and also includes a new or improved colour development process which consists in developing a reducible silver salt image in a photographic element with the aid of an aromatic amino compound in presence of a colour coupler as hereinafter defined as well as the colour photographic elements resulting therefrom. It also includes photographic sensitive elements having such a colour coupler incorporated in one or more emulsion layers.

50 The silver can be removed from the image after colour development leaving a clear transparent dye image.

The invention also includes a photographic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling *in situ*, during development of a developable silver salt, of a colour coupler as hereinafter defined with the oxidation product of an aromatic amino developer agent.

60 When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent

is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour couplers during development to form dyes. If such colour couplers are added to the developer solution, or incorporated in the emulsion layer, the dye which is thus formed by coupling during development is deposited in the gelatine or other silver halide carrier adjacent to the metallic silver grain. It is desirable that the dyes thus formed should not readily wander from the place of formation. It is accordingly, desirable that they should be insoluble in water. They are probably not physically attached to the silver grain. The silver may be subsequently bleached out of the carrier layer leaving a pure dye image.

Numerous substances have hitherto been employed or proposed as colour couplers among which may be mentioned phenols, naphthols, cresols, nitrophenylacetonitrile and acetoacetic esters. It has not, however, always been possible among those hitherto available to select one which exhibits all the desired combination of properties required for any specific case. In colour-developing a gelatino-silver halide emulsion layer it is necessary to select a colour coupler which will give just the desired shade in conjunction with the colours which are produced in other layers. It is moreover important to employ a colour coupler which gives a coloured compound which is resistant to the normal processing baths employed, although it may often be desirable to have one which gives a colour which can be destroyed and/or removed if desired during some step in the processing. Many of the colour couplers employed according to the present invention are suitable in carrying out the processing described in our prior Patents Nos. 427,472, 427,516, 427,518, 427,520, 440,032, 440,089, and 447,092.

According to the present invention the substances employed as colour couplers are compounds having the group



directly attached to one ring of a group containing at least two closed rings. These compounds may therefore be termed cyanacetyl derivatives of bicyclic compounds. The group containing at least two closed rings may be, for example, a naphthyl group, an acenaphthenyl group, a dibenzofuryl group, a coumaronyl group or a phenoxyphenyl group. Typical examples of suitable couplers are:—

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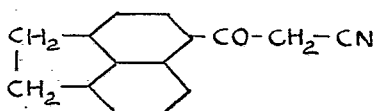
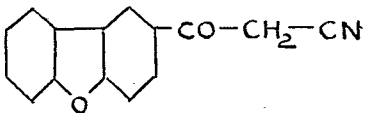
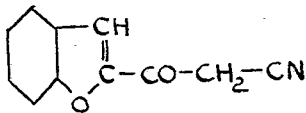
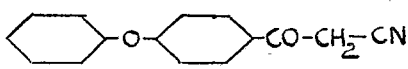
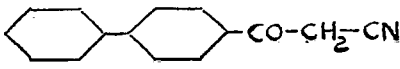
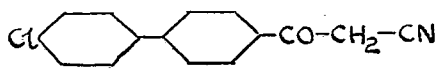
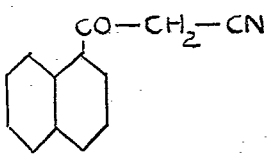
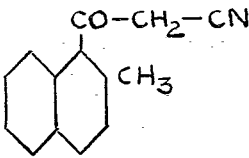
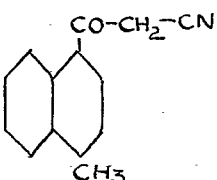
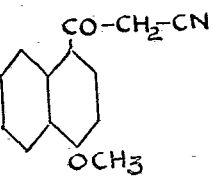
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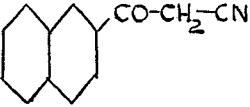
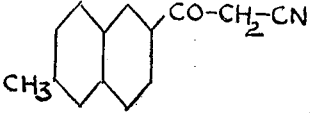
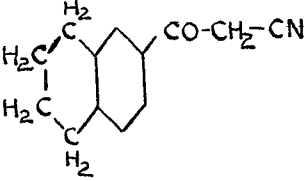
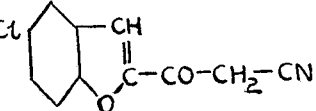
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1.  3- ω -Cyanacetyl-acenaphthene
2.  3- ω -Cyanacetyl-dibenzfuran
3.  1-(ω -Cyanacetyl)-coumarone
4.  *p*-Phenoxybenzoyl-acetonitrile
5.  *p*-Phenylbenzoyl-acetonitrile
6.  *p*-(p^1 -Chlorophenyl)benzoyl-acetonitrile
7.  α -Naphthoylacetonitrile
8.  2-Methyl- α -naphthoylacetonitrile
9.  4-Methyl- α -naphthoylacetonitrile
10.  4-Methoxy- α -naphthoylacetonitrile

11.  β -Naphthoylacetonitrile
12.  6-Methyl-2-naphthoylacetonitrile
13.  Tetrahydro- β -naphthoylacetonitrile
14.  1- ω -Cyanoacetyl-4-chlorocoumarone

These compounds, when present during the development of a silver salt with an aromatic amino developing agent, couple with the oxidation product of such developing agent forming a dye simultaneously with the formation of the silver image. The coupling occurs in each case at the methylene group contained between the carbonyl group and the cyano group

of the coupler.

To prepare α -naphthoylacetonitrile, α -naphthacyl chloride was prepared in the manner described by Schroeter, Müller, Huang, Ber. 62, 655 (1929). It melted at 37—39° C. In a similar manner the following halogenated methyl ketone derivatives were obtained which had the physical constants indicated:—

- 20 3- ω -Chloroacetyl-dibenzfuran (referred to as 2-chloro acetyl-dibenzfuran in J.A.C.S. 57, 1124 (1935))
p-(*p*-Chlorophenyl)phenacyl bromide
 4-Methoxy-1-chloroacetyl naphthalene
 2-Methyl-1-chloroacetyl naphthalene
 25 *p*-Phenylphenacyl chloride
 3- ω -Chloroacetylacenaphthene
p-Phenoxyphenacyl chloride.
 4-Methyl-1-chloroacetylnaphthalene
- M.P. 106—108° C.
 M.P. 126—127° C.
 M.P. 69—70° C.
 M.P. 190—195° C./8 mm.
 M.P. 127—128° C.
 (Ber. 53, 295 1920)
 Oil which could not be distilled.
 B.P. 197—202° C./11 mm.

The following bromoketones were obtained by bromination of the corresponding methyl ketones in chloroform,

carbon tetrachloride or other inert solvent.

- 35 β -Naphthacyl bromide (Roczniki Chem, 9, 538 (1929))
 1- ω -Bromoacetyl coumarone (Ann. 312, 332)
 6-Methyl-2-naphthacyl bromide (from 6-methyl-2-acetonaphthalene, Roczniki Chem. 12, 693 (1932))

6-(ω -Chloroacetyl) tetrahydronaphthalene was prepared according to directions of Rabcewicz - Zubkowski, Roczniki Chem., 14, 160 (1934) by action of chloroacetyl chloride on tetrahydronaphthalene in carbon disulphide in presence of

aluminium chloride. The product melted at 60—62° C.

The corresponding cyanomethyl ketone derivatives were prepared from the above halogenated ketones by adding a warm aqueous solution of 3 molecular amounts

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of sodium or potassium cyanide to a warm alcohol solution of the halogenated ketone and heating for $\frac{1}{2}$ to $1\frac{1}{2}$ hours on a steam bath. The product was obtained by pouring the resulting reaction mixture

into 3 volumes of dilute acid and recrystallizing the resulting crude material from a suitable solvent.

The products and their melting points are as follows:—

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	<i>α</i> -Naphthoylacetonitrile	M.P. 100—101° C.
	3- <i>ω</i> -Cyanoacetyl dibenzfuran	M.P. 133—135° C.
	<i>p</i> -(<i>p</i> ¹ -Chlorophenyl)benzoylacetonitrile	M.P. 171—173° C.
	4-Methoxy- <i>α</i> -naphthoylacetonitrile	M.P. 180—182° C.
15	2-Methyl- <i>α</i> -naphthoylacetonitrile	M.P. 93—95° C.
	<i>p</i> -Phenylbenzoylacetonitrile	M.P. 99—101° C.
	3- <i>ω</i> -Cyanoacetyl-acenaphthene	M.P. 160—162° C.
	<i>p</i> --Phenoxybenzoylacetonitrile	M.P. 85—86° C.
	4-Methyl- <i>α</i> -naphthoylacetonitrile	M.P. 85—88° C.
20	<i>β</i> -Naphthoylacetonitrile	M.P. 125—126° C.
	1- <i>ω</i> -Cyanoacetyl coumarone	M.P. 151—152° C.
	6-Methyl-2-naphthoylacetonitrile	M.P. 159—160° C.
	Tetrahydro-6-naphthoylacetonitrile	M.P. 98—100° C.

1-Acetyl-4-chlorocoumarone (M.P. 98—100° C.) is prepared in a manner similar to that described by Stormer, Ber. 30, 1711. It is brominated in a suitable solvent such as methyl alcohol or chloroform to give 1-*ω*-bromoacetyl-4-chlorocoumarone (M.P. 111—113° C.)

One molecular amount of this bromo-derivative is added with good stirring to a warm (50° C.) alcoholic suspension of two molecular parts by weight of sodium cyanide. The sodium salt of the cyanoketone which separates is filtered off and dissolved in cold water. Upon acidifying the aqueous solution, the 1-*ω*-cyanoacetyl-4-chlorocoumarone separates in fairly pure form. After filtering, washing with water and drying, the product melts at 127—129° C.

The colour couplers, as illustrated above, may be substituted in one or more of the rings. The substituent groups may include halogen, nitro, amino, substituted amino, aryl, and carboxyl groups. The substituent groups may be in any position in the rings since these rings are not reactive in the coupling to form the dye.

The aromatic amino compounds which may be used as developing agents in the

present invention include the mono-, di-, and tri-amino aryl compounds. Among the monoamino compounds may be mentioned the amino-phenols and aminocresols and their halogen substituted derivatives as well as the aminonaphthols. The developing agents usually used are the diamino compounds such as para-phenylene diamine and its substitution products. These developing agents may be substituted in the amino group or in the ring or in both, forming compounds such as the alkyl phenylene diamines, toluylene-diamines, alkyl-toluylene diamines and aminodiphenylamines. These compounds are usually kept in the salt form such as hydrochloride or sulphate since these are more stable than the amines themselves. As examples of developing agents of this class, there may be mentioned diethyl para-phenylene diamine, mono-methyl para-phenylene diamine, dimethyl para-phenylene diamine and ortho-amino-diethylaniline. As would be expected from the behaviour of known colour couplers the shade of the colour obtained by coupling generally varies in accordance with the developing agent selected.

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EXAMPLE.

85 A developing formula which may be used is the following:—

	A			
	Diethyl para phenylenediamine	-	-	1 gram
	Sodium sulphite	-	-	0.5 gram
	Sodium carbonate	-	-	20 grams
90	Water	-	-	1 litre
	B			
	Colour coupler	-	-	The molecular equivalent of the developing agent
95	Water miscible solvent such as acetone	-	-	50 cc.

For use, B is added to A.

The developing agent and the proportions of the ingredients used in the above formula may, of course, be varied. Solvents other than acetone, such as alcohols, may also be used.

The colours formed by the compounds named above on coupling with the oxidization product of the developer are various shades of red and magenta. The colours of dyes formed from couplers having substituents in the rings may vary according to the type of substituent group employed.

Although we have described our invention with particular reference to the use of the colour coupler in the developing solution itself, our invention is in no way limited to this method. As an alternative method, the colour coupler may be incorporated in the photographic layer before development, and either before or after exposure. It may be absorbed upon the sensitive silver halide grains.

The present invention may be utilised in the formation of coloured photographic images on plates or papers as well as on films and employing gelatine or other carrier for the silver halide. The plates, films or papers may have differently sensitized emulsions of the mixed grain type or superimposed on one side or on both sides of the support. The dyes formed may be decolorized by an oxidizing agent such as chromic acid and colourless soluble compounds thereby formed. The bleaching of the dye in this manner need not destroy the silver image but may convert it into a developable silver salt image which can in turn be coloured, bleached and recoloured a number of times.

The present invention makes available a range of compounds which have important advantages over those hitherto known and used. For example, β -naphthoyl-acetonitrile gives rise to a colouring matter with much improved sharpness of absorption as compared with that obtained from the known compound benzoyl-acetonitrile. 1- ω -cyanoacetylcoumarone is very much more stable in the developer solution than thioindoxyl, which has similar absorption characteristics. The latter couples spontaneously with great rapidity, thus exhausting the solution.

The absorption characteristics of these compounds are illustrated in the accompanying drawings. These drawings represent graphs in which the density of the coloured image is represented on the ordinate and the wave lengths on the abscissa.

In Figure 1 Curve A gives the absorption characteristics of the dye formed, using 2-amino-5-diethylaminotoluene as

the developing agent, and benzoyl-acetonitrile as the coupler, and Curve B gives the absorption characteristics of the dye formed, when using the same developing agent but β -naphthoyl-acetonitrile as the coupler. It will be seen that the absorption band with the naphthoyl compound is much sharper.

In Figure 2 Curve C shows absorption characteristics of the dye obtained with para-aminodiethylaniline as the developing agent, and thio-indoxyl as the coupler. Curve D shows the absorption characteristics of the dye obtained with the same developing agent but with 1- ω -cyanoacetylcoumarone as the coupler.

It will be seen that although thio-indoxyl shows a higher over-all absorption, it does not have a sharper absorption band. As has already been pointed out, 1- ω -cyanoacetylcoumarone has the substantial advantage over thioindoxyl of being more stable in solution.

We do not claim, in this application, a colour forming developer containing β -naphthoyl-acetonitrile as the colour former and formaldehyde sulphoxylate or hydrazine or hydroxylamine as a preservative. Colour developers containing these latter substances as preservatives are claimed in Specification No. 462,140.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to us by our foreign correspondents, we declare that what we claim is:—

1. A colour forming developer comprising an aromatic amino developing agent and a colour coupler having the group



directly attached to one ring of a group containing at least two closed rings (subject to the foregoing disclaimer).

2. A colour forming developer as claimed in Claim 1 in which the group containing at least two closed rings is a naphthalene group.

3. A colour forming developer as claimed in Claim 1 or 2, in which the developing agent is an aromatic diamino compound.

4. A colour forming developer as claimed in Claim 3, in which the aromatic diamino compound is an alkyl substituted phenylene diamine.

5. A process of colour development which includes developing a reducible silver salt image with an aromatic amino developing agent in presence of a colour coupler as defined in Claim 1.

6. A process of colour development

which includes developing a reducible silver salt image with a colour forming developer as claimed in any of Claims 1 to 4.

5 7. A photographic element having a layer containing a clear transparent dye image composed essentially of the product resulting from the coupling *in situ*, during development of a developable silver salt, of a colour coupler as defined in 10 Claim 1 or 2 with the oxidation product of an aromatic amino developing agent and subsequent removal of metallic silver.

15 8. A sensitive photographic element having a colour coupler as defined in Claim 1 or 2 incorporated in one or more emulsion layers.

9. The colour forming developers and methods of colour development employing the colour couplers hereinbefore particularly described, in conjunction with aromatic amino developing agents. 20

10. In the production of colour photographic records especially multi-layer records, the employment in conjunction with aromatic amino developing agents of colour couplers of the nature herein defined (subject to the foregoing disclaimer). 25

Dated this 21st day of April, 1937.

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

[This Drawing is a reproduction of the Original on a reduced scale.]

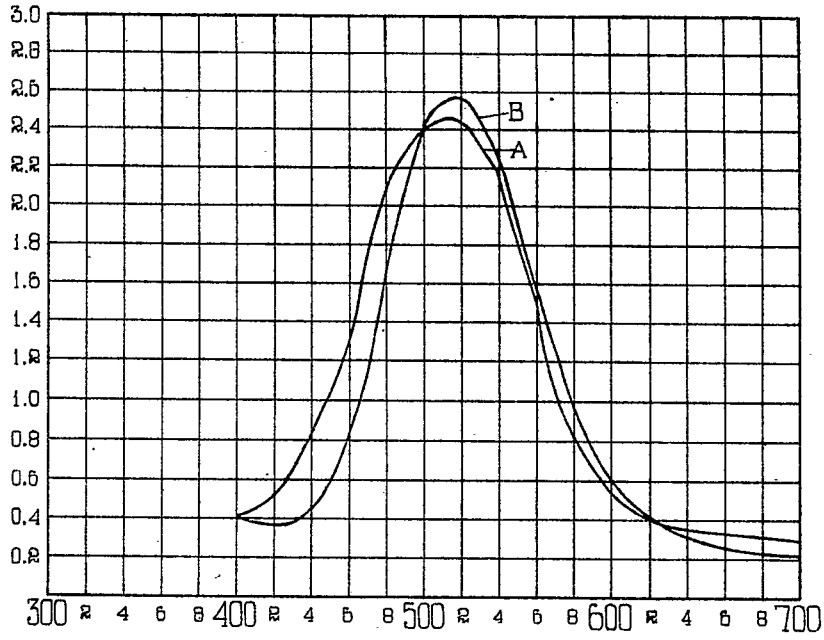


FIG. 1.

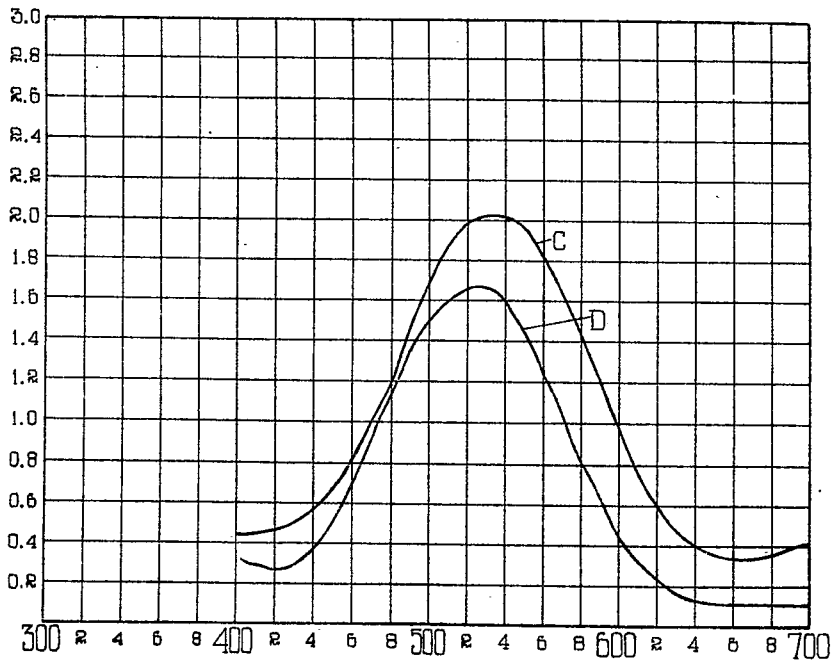


FIG. 2.