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PATENT SPECIFICATION

Application Date: April 23, 1936. No. 14353/37.

478,990

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Complete Specification Left: May 24, 1937.

Complete Specification 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.

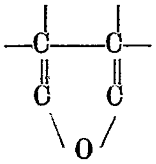
When a silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour 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, nitrophenylacetonitriles 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

[*Price* 1/-]

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 heterocyclo-substituted pyrazolones, 5-imino-pyrazolones, 5-thiopyrazolones, 3-hydroxypyrazolones and 3-carboxypyrazolones, compounds having a reactive methylene group and containing the grouping—



or thiazole derivatives containing in a substituent grouping a phenolic hydroxyl group or a reactive methylene group.

Examples of such colour couplers are:—

1. 3-furyl-5-pyrazolone.
2. 1-phenyl-3-furyl-5-pyrazolone.
3. 1-(2^1-benzthiazolyl)-3-methyl-5-pyrazolone.
4. 1-phenyl-3-carboxylic acid-5-pyrazolone.
5. 1-phenyl-3-carboxylic acid methyl ester-5-pyrazolone.
6. 1-*o*-chlorophenyl-3-carboxylic acid-5-pyrazolone.
7. 1-(8^1-quinolyl)-3-methyl-5-pyrazolone.
8. 1-(2^1-quinolyl)-3-methyl-5-pyrazolone.
9. 1-phenyl-3-hydroxy-5-pyrazolone (2-phenyl-3:5 diketopyrazolone).
10. 1-phenyl-3-hydroxy-5-imino-pyrazolone.
11. 1-phenyl-3-methyl-5-thiopyrazolone.

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

1-phenyl-3-carboxylic acid methyl-ester-5-pyrazolone (blue).

1 - phenyl - 3 - hydroxy - 5 - pyrazolone (orange).

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 and aminocresols and their halogen substituted derivatives as well as the aminonaphthols. The developing agents usually used are the diamino compounds such as paraphenylene 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. 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.

The present invention may be utilised in the formation of coloured photographic images on plates or papers 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.

Dated this 21st day of May, 1937.

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

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, and in what manner the same is to be performed, to be particularly described and ascertained 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.

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 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.

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 the developable silver salt, of a colour coupler as hereinafter defined with the oxidation product of an aromatic amino developer agent.

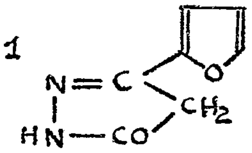
When the silver halide emulsion containing a latent photographic image is developed, the silver halide is reduced to metallic silver and the developing agent is oxidized. The aromatic diamino compounds which have been used as developing agents form, on oxidation, products which will couple with colour 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, nitrophenylacetonitriles 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 heterocyclo-substituted pyrazolones, 5-imino-pyrazolones, 5-thiopyrazolones, 3-hydroxypyrazolones and 3-carboxypyrazolones.

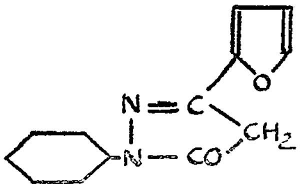
Typical examples of suitable couplers are:—

1



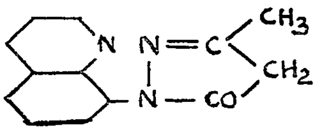
3-furyl-5-pyrazolone

2.



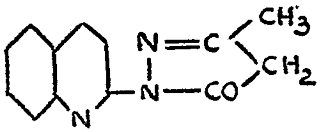
1-phenyl-3-furyl-5-pyrazolone

3.



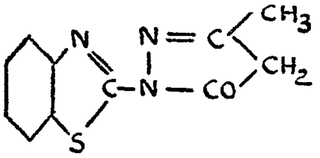
1-(8^1-quinolyl)-3-methyl-5-pyrazolone

4.



1-(2^1-quinolyl)-3-methyl-5-pyrazolone

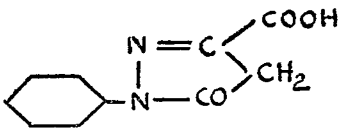
5.



1-(1^1-benzthiazolyl)-3-methyl-5-pyrazolone

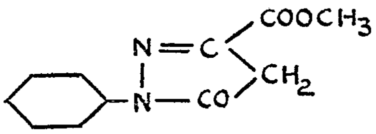
The above couplers are preferred in the practice of our invention. Others which can be employed but which are less useful are the following.

6.



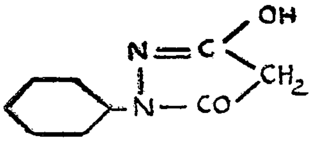
1-phenyl-3-carboxylic acid-5-pyrazolone

7.



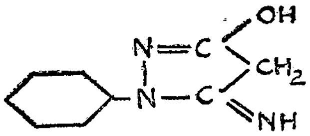
1-phenyl-3-carboxylic acid methyl ester-5-pyrazolone

8.



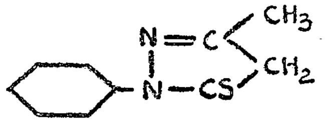
1-phenyl-3-hydroxy-5-pyrazolone (2-phenyl-3-diketopyrazolone)

9.



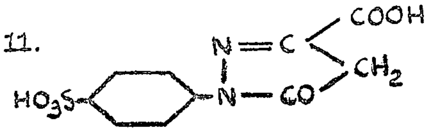
1-phenyl-3-hydroxy-5-imino-pyrazolone

10.



1-phenyl-3-methyl-5-thiopyrazolone

11.



1-*p*-sulphophenyl-3-carboxylic acid-5-pyrazolone.

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.

3-furyl-5-pyrazolone was prepared by the directions given by Torrey and Zanetti Am. Chem. J. 36, 539; and 44, 412, (1910).

1-phenyl-3-furyl-5-pyrazolone was prepared by the re-action of equimolecular amounts of phenylhydrazine and ethyl furoylacetate in dilute alcohol solution. The product melted at 180—181° C.

1-phenyl-3-carboxylic acid methyl ester-5-pyrazolone was prepared from methyl oxalacetate and phenylhydrazine in the manner used by Wislicenus and Reitzenstein Ann. 277, 378 (1893).

Ethyl β-(1-benzothiazolyl hydrazone) butyrate was prepared by the re-action of 1-benzothiazolylhydrazine with ethyl acetoactate in acetic acid solution. The product was recrystallized from dilute alcohol and melted at 108—109° C.

Upon heating the above mentioned hydrazone in an indifferent solvent (such as Xylene) 1-(1^1-benzthiazolyl)-3-methyl-5-pyrazolone was formed. It melted at 226—227° C.

1 - (2^1 - quinolyl) - 3 - methyl - 5-pyrazolone was prepared in the manner described by Fargher and Furness in J.C.S. 107, 699 (1915) and melted at 139—140° C.

1-phenyl-3-hydroxy-5-pyrazolone was prepared in the manner described by Conrad and Zart in Ber. 39, 2283 (1906).

1 - phenyl - 3 - hydroxy - 5 - imino-pyrazolone was prepared in accordance with the directions of Conrad and Zart in Ber. 39, 2287 (1906).

1-*p*-sulphophenyl-3-carboxylic acid-5-pyrazolone (sodium salt) was synthesized according to the directions of Anschütz in Ann. 294, 232 (1907).

1 - (8^1 - quinolyl) - 3 - methyl - 5-pyrazolone was prepared as follows by condensation of 8-quinolylhydrazine with ethyl acetoacetate. 8-quinolylhydrazine was made by diazotization of 8-amino-quinoline and reduction of the diazonium salt. Details are as follows:—

8-Quinolylhydrazine.

In a one-litre beaker surrounded by a salt-ice mixture, 15 gms. (0.108 gm.-mol.) of 8-amino-quinoline were added to a mixture of 250 cc. conc. hydrochloric acid and 150 gms. of ice. The resulting solution was chilled to 0° C. and then 35 cc. (0.1 gm.-mol.) of a 20% sodium nitrite solution were added very slowly over a period of 15 minutes to the stirred solution, keeping the temperature below 3° C. To the diazotized solution was added with stirring a solution of 45 gms. (0.24 gm.-mol.) of stannous chloride in 65 cc. conc. hydrochloric acid. The mixture was then allowed to stand for one day. To the suspension was added sodium chloride and, after standing for one hour, the solid was filtered off and pressed as dry as possible. The solid was then added to one half its volume of ice and the mixture made distinctly alkaline with 20% caustic soda solution keeping the solution cold (10°—15° C.), then extracted several times with 250 cc. portions of ether. The combined extracts were dried over anhydrous sodium sulphate, filtered and concentrated to approximately 20 cc. The solution on cooling went solid and was washed with a mixture of equal parts ether and petroleum ether. The product was filtered by suction and then dried in the open air. It melted at 137°—139° C. A further yield of product was obtained by rendering the original filtrate alkaline extracting it with ether and treating the extract similarly.

1-(8^1-QUINOLYL)-3-METHYL-5-PYRAZOLONE.

In a 50 cc. Erlenmyer flask, 2 gms. (0.0125 gm.-mol.) of 8-quinolylhydrazine were treated with a solution of 1.8 gms. (0.0138 gm. mol.) of ethyl acetoacetate dissolved in 3.5 cc. acetic acid and allowed to stand over night at room temperature. The solid which had separated out was filtered off and washed well with methyl alcohol and dried in a hot air oven. The product melted at 256—258° C.

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 and aminocresols and their halogen substituted derivatives as well as the amino-naphthols. 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.

EXAMPLE.

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

A.

Diethyl para phenylene-diamine - - - - -	1 gram
Sodium sulphite - - -	0.5 gram
Sodium carbonate - - -	20 grams
Water - - - - - - -	1 litre

B.

Colour coupler - - -	The molecular equivalent of the developing agent.
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 be also used.

The colours formed by the compounds named above on coupling with the oxidization product of the developer are magenta except in the case of compound No. 7 which gives blue and compound No. 8 which gives orange. The colours of dyes formed from couplers having further substituents 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 utilized in the formation of coloured photographic images on plates or papers as well as on films 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 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.

The accompanying drawings show the absorption characteristics of the dyes formed from two of the couplers of the present invention. The drawings are graphs in which the density of the coloured image is represented on the ordinate and wave lengths on the abscissa. In Figure 1 the coupler is 1-Phenyl-3-furyl-5-pyrazolone. In Figure 2 the coupler is 1-(1^1-Benzthiazolyl) - 3 - methyl-5-pyrazolone.

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 consisting of a heterocyclo-substituted pyrazolone, a 5-imino-pyrazolone, a 5-thiopyrazolone, a 3-hydroxypyrazolone or a 3-carboxypyrazolone.

2. A colour forming developer as claimed in claim 1 in which the colour coupler consists of a heterocyclo-substituted pyrazolone wherein the heterocyclic substituent is a furan, quinoline or benzthiazole nucleus.

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 sub-

stituted 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 or 2.

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.

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 claim 1 or 2, with the oxidation product of an aromatic amino developing agent and subsequent removal of metallic silver.

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.

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.

Dated this 21st day of May, 1937.

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.—1938.

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

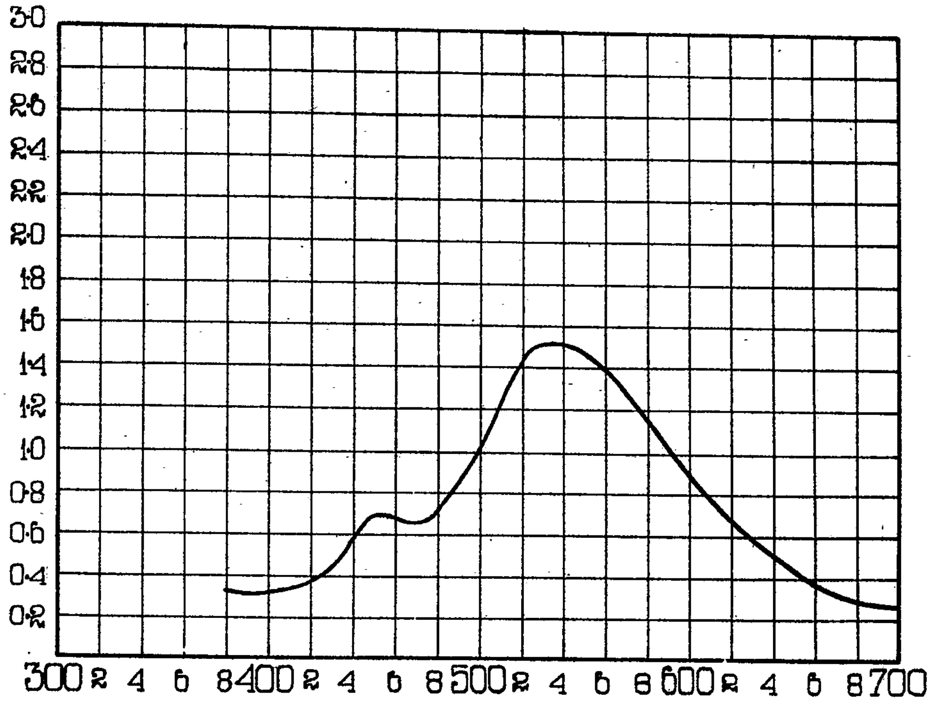


Fig. 1.

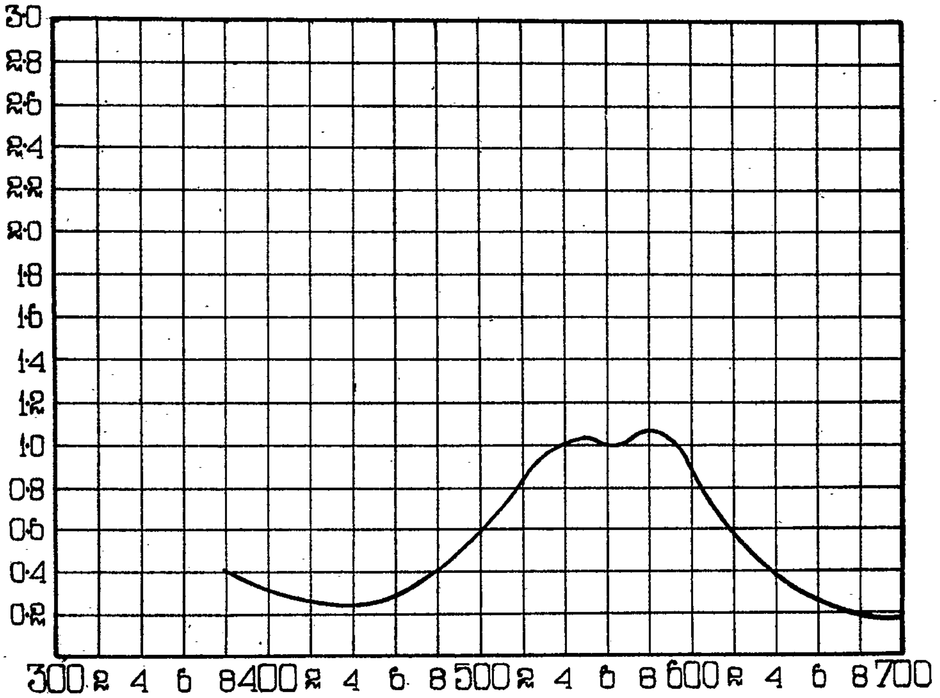


Fig. 2.

Malby & Sons, Photo-Litho