

PATENT SPECIFICATION



Application Date: April 23, 1937. No. 11621/37.
 (Patent of Addition to No. 458,664: dated March 21, 1935.)

493,952

Complete Specification Left: April 25, 1938.

Accepted: Oct. 18, 1938.

PROVISIONAL SPECIFICATION

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

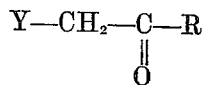
We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention, which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New Jersey, United States of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

5
10

This invention relates to colour forming developers and to processes of colour development for use in connection with colour photography and in particular to improvements in or modifications of the invention described and claimed in the parent specification No. 458,664.

15

According to the parent specification the substances employed as colour couplers 20 are organic compounds with a reactive methylene group having the general formula



where

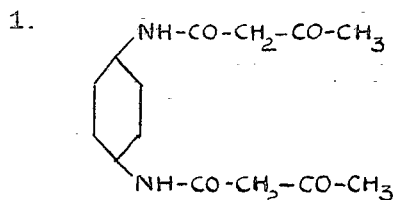
Y = one of the electro-negative groups CN— or X.CO— (where X is an alkyl or aryl group, substituted or unsubstituted).

R = an aryl- or heterocyclo-substituted amino group.

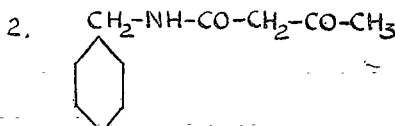
According to the present invention the compounds employed as colour couplers are:—

25

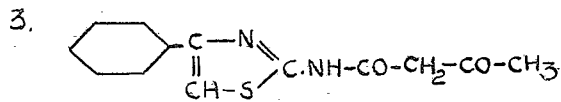
30



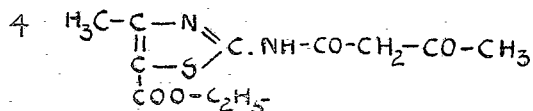
1 : 4-Di-(acetoacetamino)-benzene.



Acetoacetbenzylamide.



2-acetoacetamino-4-phenylthiazole

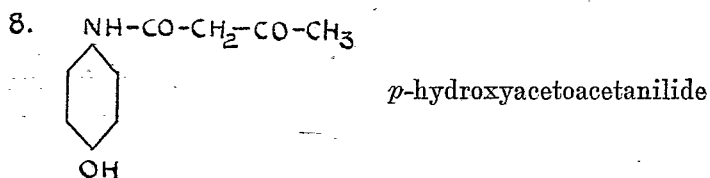
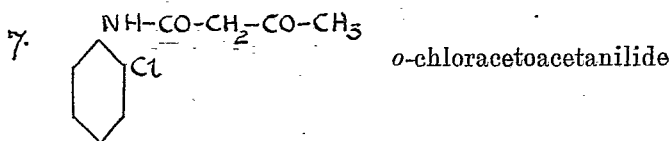
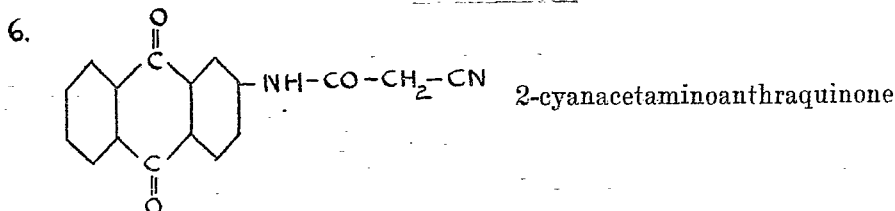
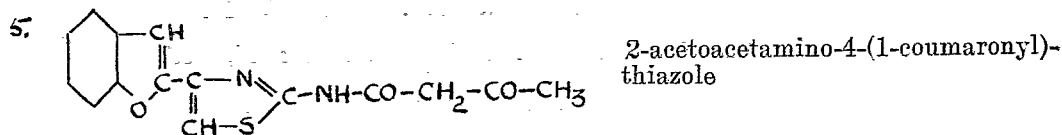


2-acetoacetamino-4-methyl-5-carbethoxythiazole

[Price 4s]

Price 4s 6d

Price 4s 6d



The colours produced by the above named couplers when developed with *p*-amino-diethyl aniline as developing agent are yellow except in the case of 5 No. 6 which yields a reddish dye.

Dated this 21st day of April, 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:—

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

in particular to improvements in or modifications of the invention described and claimed in the parent specification No. 458,664. 25

It is known that coloured photographic images may be formed by using a developing agent which forms a coloured compound on development of a silver salt. 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 photographic silver halide emulsion before or after exposure a compound which couples, during development, with the oxidation product of the developing agent, 30 35 40

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 developing agent 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.

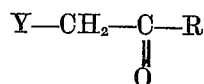
The invention also includes a photographic element having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling, *in situ* during development of a developable silver salt, of a colour coupler as hereinafter defined with the oxidation product 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 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, nitrophenylacetone nitriles 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 gelatin-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 inventions are suitable in carrying out the processing described in our prior specifications Nos. 427,472, 427,516, 427,520, 440,032, 440,089, 447,092, 475,784 and 475,786.

According to the parent specification the substances employed as colour couplers are organic compounds with a reactive methylene group having the general formula

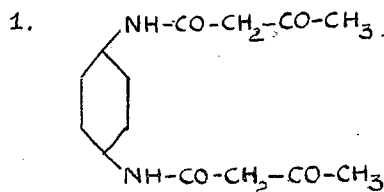


where

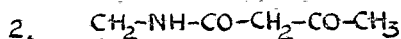
Y=one of the electro-negative groups CN— or X.CO— (where X is an alkyl or aryl group, substituted or unsubstituted).

R=an aryl- or heterocyclo-substituted amino group.

According to the present invention the compounds employed as colour couplers are:—

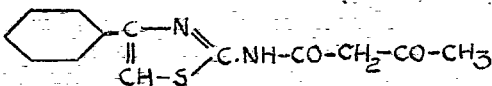


1:4-Di-(acetoacetamino)-benzene

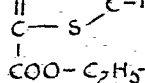


Acetoacetbenzylamide.

3.

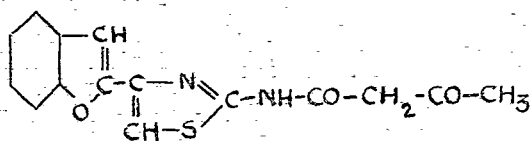


2-acetoacetamino-4-phenylthiazole



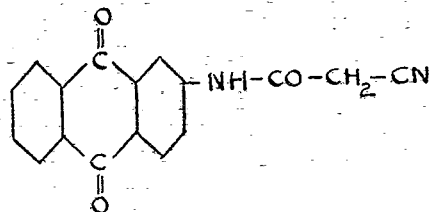
2-acetoacetamino-4-methyl-5-carbomethoxythiazole

5.



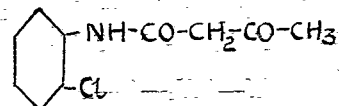
2-acetoacetamino-4-(1-coumaronyl)thiazole

6.

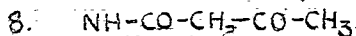


2-cyanacetaminoanthraquinone

7.



o-chloroacetoacetanilide



p-hydroxyacetoacetanilide

The colours produced by the above named couplers when developed with *p*-amino-diethyl aniline as developing agent are yellow except in the case of 5 No. 6 which yields a reddish 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 aminophenols, 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 groups or in the ring or in both, forming compounds such as the alkyl-phenylenediamines, toluylene-diamines, 15 alkyl-toluylenediamines 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-phenylenediamine, mono-methyl-para-phenylenediamine, dimethyl-para-phenylenediamine and ortho-amino-diethylaniline.
- As would be expected from the behaviour of known colour couplers the shade of colour obtained by coupling generally varies in accordance with the developing agents selected.
- A developing formula which may be used is the following:—
- A.
- | | | | |
|----|-------------------------------|----------|--|
| | Diethyl- <i>p</i> -phenylene- | | |
| | diamine hydrochloride | 1 gram | |
| 20 | Sodium sulphite - - | 0.5 gram | |
| | Sodium carbonate - - | 20 grams | |
| | Water to - - - - | 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 also be used.
- 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 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 when 2-acetoacetamino-4-methyl-5-carbethoxythiazole (Figure 1) and 2-acetoacetamino-4-phenylthiazole (Figure 2) are used respectively as the colour couplers. The figures of the drawing are graphs on which the density of the coloured image is represented on the ordinate and wave lengths on the abscissa.
- 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:—
- The improvement in or modification of the invention claimed in the parent patent No. 458,664 in which the colour coupler is one of the compounds 1 to 8 hereinbefore named.
- Dated this 23rd day of April, 1938.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

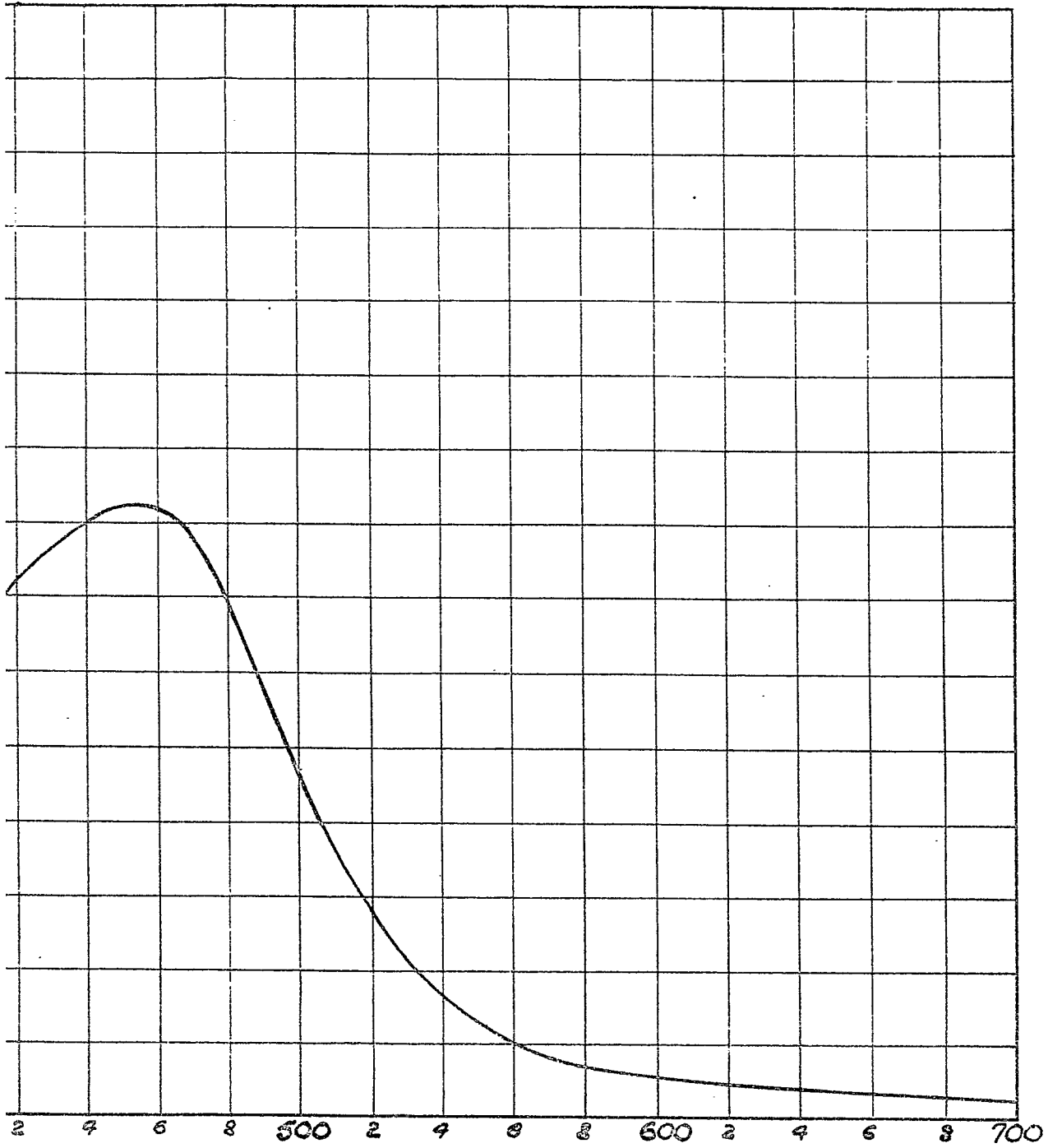


FIG. 1.
0

493,952 COMPLETE SPECIFICATION

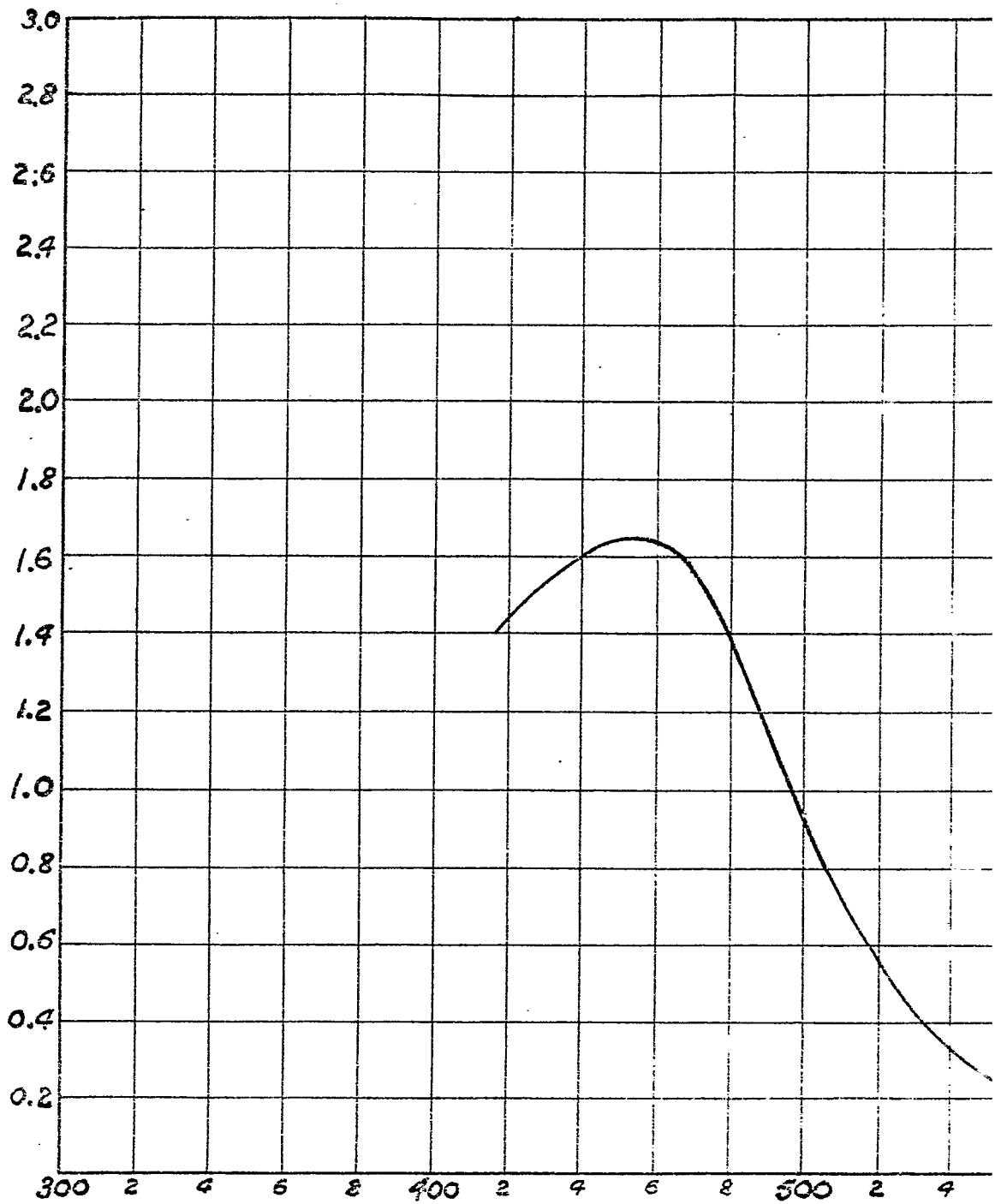
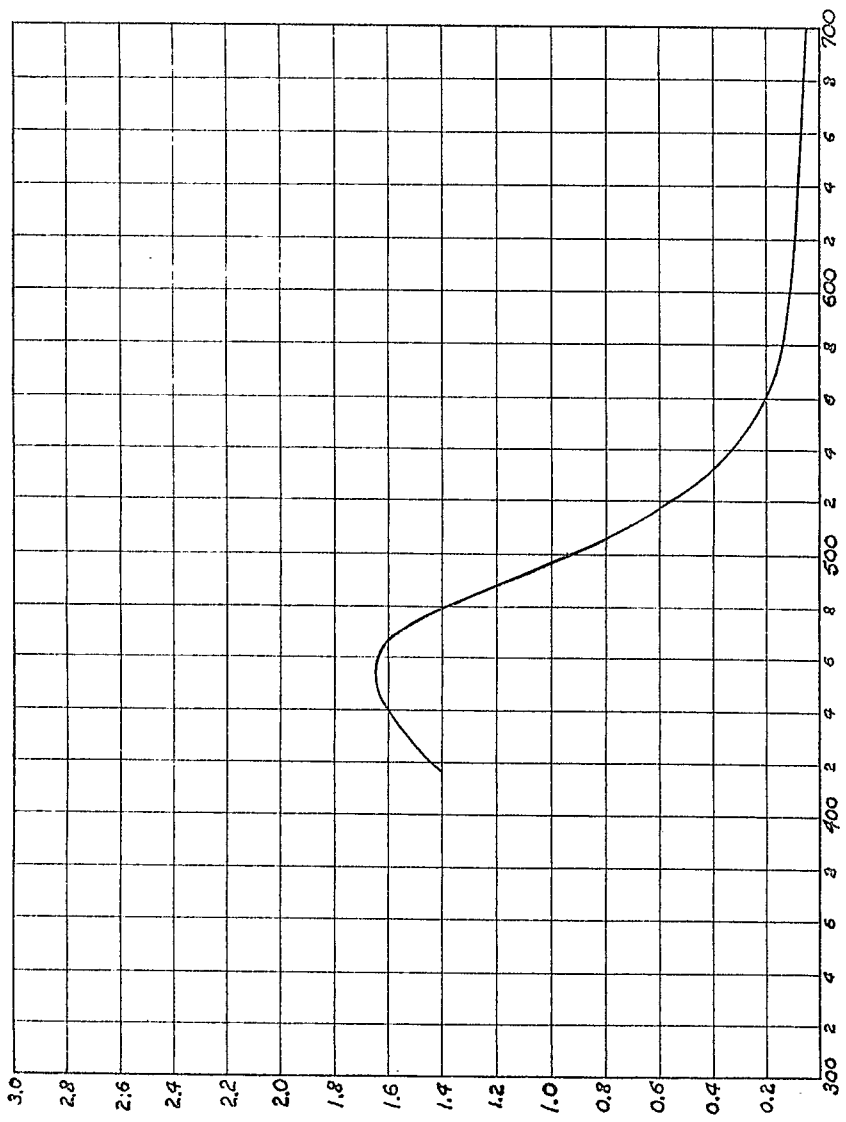


FIG. 1.
O



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

Fig. 9

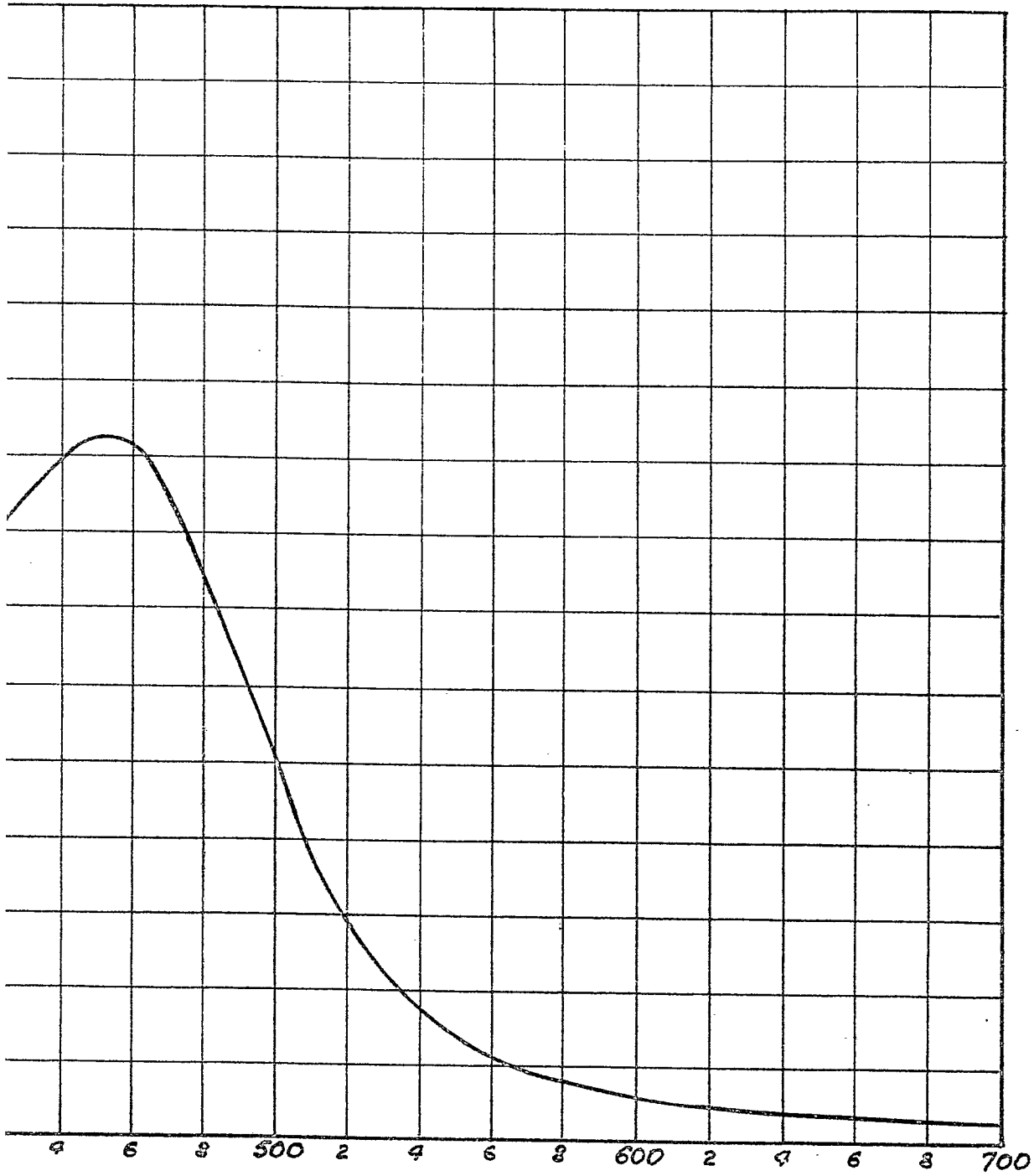


FIG. 2.

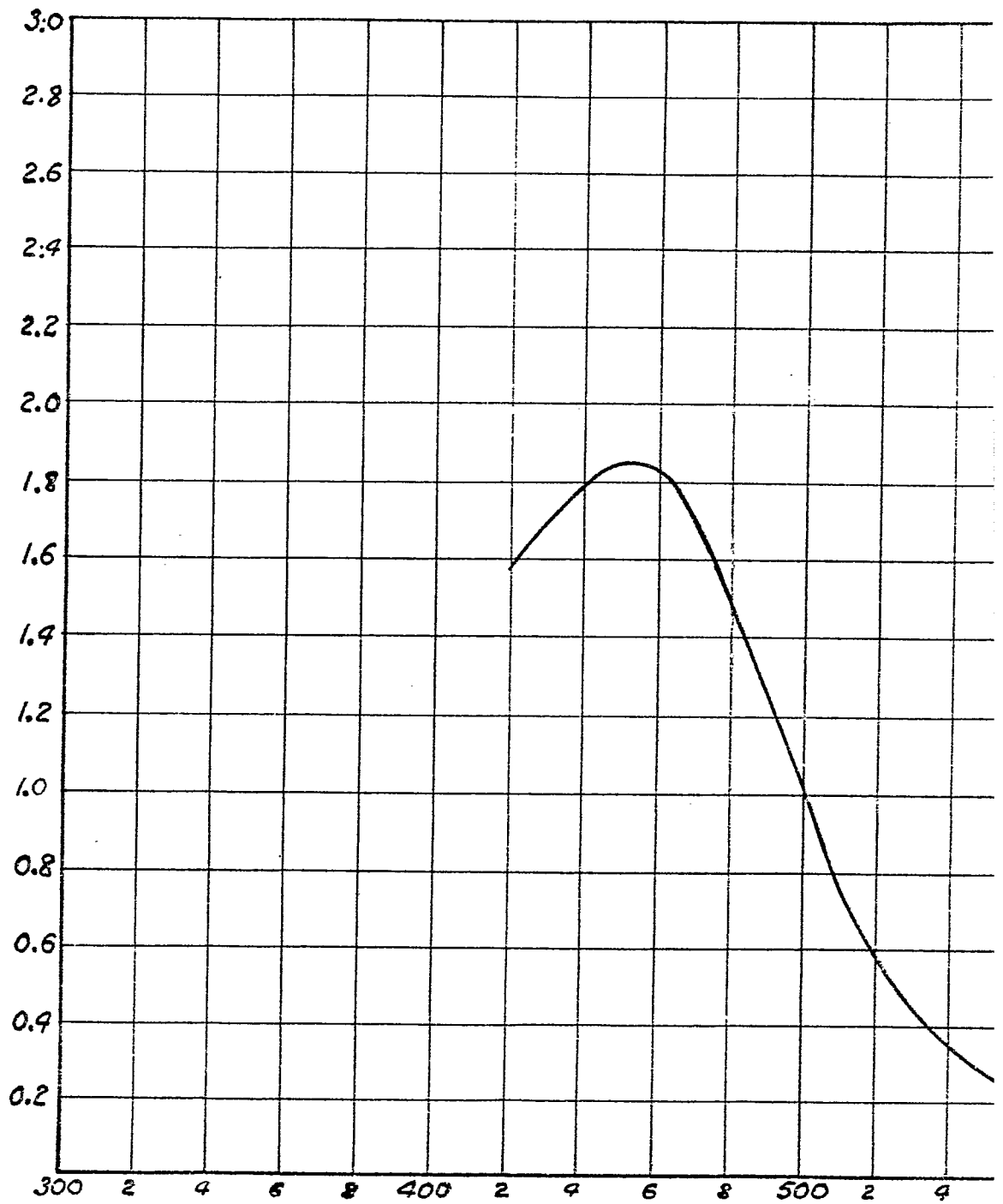


FIG. 2.

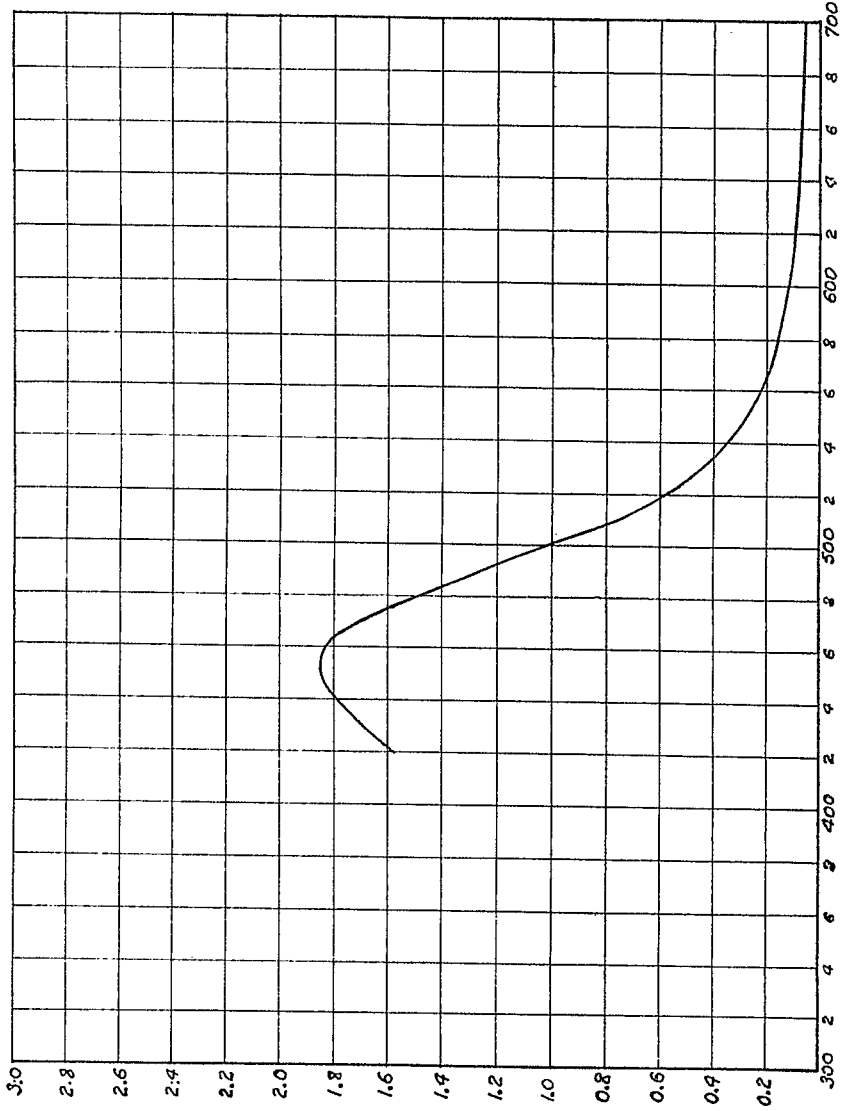


Fig. 2.

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