

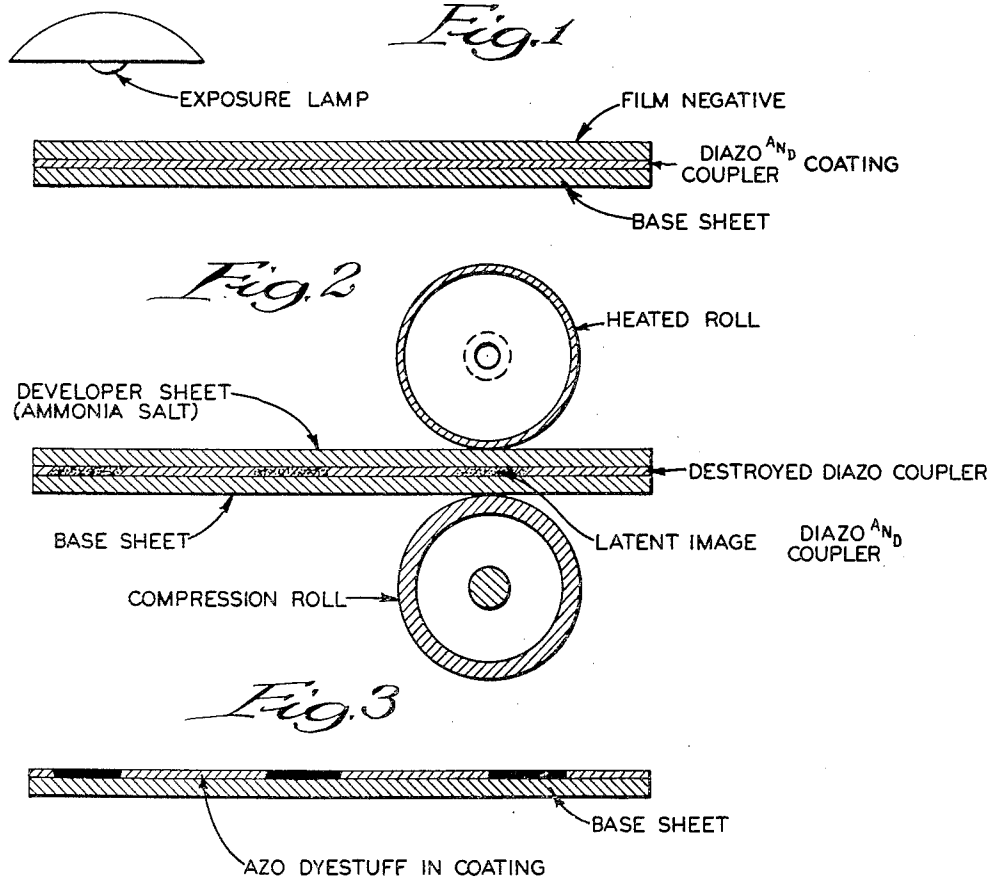
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DIAZOTYPE REPRODUCTION PROCESS

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DIAZOTYPE REPRODUCTION PROCESS

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1 Claim. (Cl. 96—49)

This invention relates to compositions for use in diazotype reproduction and to diazotype sheets manufactured from same and it relates more particularly to the use of said diazotype sheets to produce copy by a new and improved process adaptable for office copy work.

To the present time, diazotype reproductions are made commercially by processes known as the Ozalid or ammonia process and the Bruning or wet process, in each of which a copy sheet is used which is first sensitized with a diazo compound capable of reaction with a coupler upon adjustment of the pH to form an azo dye. In the ammonia process, the copy sheet is sensitized with the diazo and coupler. The dye forming components are destroyed upon exposure to light through a film negative leaving a latent image which is subsequently developed to form the dye color by exposure to ammonia in a gaseous chamber. In the wet process, the copy sheet contains only the diazo. The adjustment of the pH for initiating the coupling reaction to form the dyestuff of the latent image is carried out by an alkali bath.

One of the serious objections to the use of the Ozalid process for diazotype reproduction in office copy work is the necessity for using a gas chamber in which ammonia vapors can be liberated in sufficient concentration and in a desired distribution to achieve the desired conversion of the dyestuff in a rapid manner. Such gas chambers have embodied rather elaborate equipment for sealing the vapors from the outside atmosphere and for vaporizing the ammonia gas by heat from ammonium hydroxide solutions introduced into the chamber onto an evaporating pan. Operation of this type of equipment requires highly skilled labor and the high overhead makes the process impractical for the occasional production of copy in office work.

In another process represented by the Eaton Patent No. 2,597,306, a diazotype sheet of the type used in the Ozalid process is employed. The image is developed in the sheet by the application of an alkali composition such as an ammonium hydroxide solution through a stencil sheet to form the dyestuff by reaction in the copy sheet. The image is fixed and the dye forming material in the non-imaged areas of the copy sheet is destroyed by the use of light, heat or chemicals. In this process, it is necessary first to prepare a stencil containing the image as letter openings through which the alkaline fluid can be transmitted to adjust the pH for coupling in the copy sheet. The cost of stencil preparation makes this process uneconomical for use in the production of a few copies and the use of a strong alkaline solution as the stencil fluid prevents the use of duplicating machines for other copy work without the expense and time of change-over to remove the alkaline solution from the machine and replace those parts which have been substituted for purposes of resisting deterioration and attack by the strong alkaline solution.

It is an object of this invention to provide a new and improved composition for use in diazotype reproductions and it is a related object to produce and to provide

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a method for reproducing an improved sheet of the type described for use in office copy work.

Another object of this invention is to provide a diazotype reproduction process which is free of the objectionable limitations heretofore employed in such reproduction process and which can be carried out in a simple and expedient manner without the requirement of special equipment or skilled labor and which may therefore be used as an office copy process.

A further object is to provide an improved type diazo process and elements for use in the practice of same in which copy of good quality can be quickly, easily and simply produced in an economical and efficient manner and it is a related object to provide compositions for manufacture of elements used in the practice of same.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing in which—

Figure 1 is an elevational view of the arrangement of elements embodying features of this invention for developing the latent image on a diazotype sheet;

Figure 2 is a perspective view illustrating the arrangement of parts for the development of the image in the diazotype sheet, and

Figure 3 is a top plan view of the copy sheet produced in accordance with the practice of this invention.

The new and novel diazotype reproduction process embodying features of this invention requires the use of a specially prepared diazotype sheet containing the usual ingredients such as an active diazo, a diazo coupling component, and preferably an acid medium to adjust the pH of the composition to a level below that at which coupling can take place to form the dyestuff but in which other ingredients are contained whereby in coating the composition onto the base sheet, the coating positions the reactive substances in the surface where they can be made available in sufficient concentration for the formation of a dyestuff of sufficient intensity substantially instantaneously upon contact with an alkalyzing medium.

For use in combination with the diazotype sheet of the type described after it has been exposed through a film positive, there is provided a new and novel developing sheet in the form of a sheet of paper or the like coated or impregnated with a composition containing a compound or combinations of compounds which upon exposure to heat, even for a very short time, liberates ammonia or other alkalyzing vapors or fluids. While description hereinafter will be made to the use of a preferred sheet containing material to release ammonia in response to heat, it will be understood that the alkalyzing material released in response to heat may comprise other alkalyzing vapors or liquids. When the developing sheet is brought into surface contact with the coated side of the diazotype sheet during liberation of the ammonia or other alkalyzing vapors, as by passing the two sheets together between heated rolls, the existing conditions make available released alkalyzing medium to the diazotype sheet so that substantially full utilization thereof is made immediately for the purpose for which it was intended. The latent image will become developed upon being contacted with a minimum amount of vapor. As a result, it has been found possible to make use of a developing sheet of the type described over and over again for six to a dozen reproductions. The described two sheet process requires simple equipment which can be operated without highly skilled or technical assistance. Simple heated rolls or a pressing iron or the like may be used to cause the sheets to kiss as they are heated sufficiently to cause the release of vapors from one and the utilization of those vapors by the other to effect the de-

sired pH adjustment for coupling. It has been found unnecessary to take special precautions for preventing the escape of vapors out into the atmosphere, as in the gas chamber system.

It will be apparent from this brief description that there is provided for the first time a diazo reproduction process which is available for office copy work because of the possibility of carrying out the copying process without the need for highly skilled labor, without the need for expensive or complicated equipment, and without the use of compounds or materials which are dangerous in character or noticeably release objectionable amounts of substances. The process described comprises an entirely dry process making use of but two sheets of paper—one containing the latent image in the form of unreacted diazo and diazo coupling component and the other containing a compound which under special conditions releases a vapor or other alkalyzing medium in intimate contact with the imaged surface to develop the image by coupling reaction upon adjustment of the pH. The described two sheet process permits the immediate reproduction of usable copy without the necessity for drying and the developing sheet can be used repeatedly before the compounds for generating the desired alkalyzing vapors are completely destroyed.

The following examples will illustrate the manufacture of the various elements and the methods for using same in the production of copy:

Example 1

Diazotype coating composition:

60 parts para-diazo diethyl aniline zinc chloride
40 parts phloroglucinol
80 parts citric acid
80 parts zinc chloride
80 parts thiourea
25 parts 2,3-dihydroxy naphthalene 6-sodium sulfonate
800 parts water

The composition is applied by the usual coating process onto the surface of a sheet of paper, such as diazo type base paper, in amounts of about 3–8 pounds per 3000 square feet of surface area. The coating may be allowed to air dry or drying may be accelerated by exposure to elevated temperatures not higher than about 180° F.

Compositions for manufacture of developing sheet:

Example 2

40 parts ammonium formate
2–5 parts "Corpolin" (a solution of urea containing a formate, sold by Aktivin Division of Heyden Chemical company)
58 parts water

Example 3

35 parts urea
65 parts water

Example 4

30 parts $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$
70 parts water

The solutions of Examples 2–4 may be coated onto light carbonizing tissues such as Onata or Washington Linen in coating weights ranging from about 3–10 pounds per 3000 square feet of surface area.

In practice, the diazotype sheet of Example 1 is exposed to ultra violet light in contact with an original or positive or through a film negative which destroys the reactive diazo in the exposed or in the heated areas and forms a latent image therein.

After the diazotype sheet has been so exposed to form the latent image, it may be passed together with a developing sheet of the type produced by Examples 2–4 in surface contact between heated rolls of an ironer or else pressed by a heated member into surface contact with each other. The heat applied is sufficient to liberate

a small amount of ammonia from the developing sheet and force the ammonia substantially unidirectionally into or in contact with the surface of the diazotype sheet in amounts sufficient to cause adjustment of the pH for coupling reaction to form the dyestuff in the latent image. The amount of ammonia which is sufficient to effect the desired pH adjustment for the coupling reaction requires the use of only a small proportion of the available ammonia in the developing sheet so that the developing sheet may be used over and over again for the production of copy in the manner described. It will be understood that other means for introducing heat while pressing the sheets together may be employed without departing from the spirit of the invention.

Instead of the para-diazo diethyl aniline zinc chloride, various other stabilized light-sensitive diazo compounds generally referred to as active compounds may be used. These may be classified as the diazo compounds which are stable as the corresponding diazonium sulphates, chlorides, fluosilicates or fluoborates, such as para-diazo diphenylamine sulphate, diazo compounds which are stabilized as the corresponding zinc chloride or other metallic chloride salt complexes, or diazo compounds which are stabilized as salts of sulfonic acids or aryl sulfonic acids. These include:

1 diazo-2 oxy naphthalene-4 sulfonate
p-diethyl amino benzene diazonium chloride ZnCl_2
4-benzoylamino-2-5-diethoxy benzene diazonium chloride
Para-chlorobenzene-sulfonate of 4-diazo-N-cyclohexyl-aniline
Para-chlorobenzene-sulfonate of 4-diazo-2-methoxy-1-cyclohexylamino benzene
Tin chloride double salt of 4-N-methylcyclohexylamino benzene diazonium chloride
p-Acetamino benzene diazonium chloride
4-dimethylamino benzene diazonium chloride
3-methyl 4-diethyl amino benzene diazonium chloride
4-morpholino benzene diazonium chloride
4-piperidyl 2-5-diethoxy benzene diazonium chloride
1-dimethyl amino naphthalene-4-diazonium chloride

The diazo coupling component may be replaced by other compositions capable of removal of a hydrogen ion for combination with the chloride ion of the diazo dye formation. Such compounds are preferably selected of the organic compounds in the form of aromatic amines such as aniline or substituted aniline of the type dimethylaniline, or phenolic compounds such as phenol, resorcinol, phloroglucinol, 2,3-dihydroxy naphthalene 6-sulfonic acid, 1-naphthiol 4,7-disulfonic acid, 2-naphthol, 3,6-disulfonic acid, aceto acetanilide and its substitution products, phenyl methyl pyrazolone and its substitution products, thio compounds such as thio barbituric acid, or cyano compounds such as cyanoacetamide. The choice of diazo coupling component is also subject to the desired color change since one diazo coupling component will give one color with one diazo and another diazo coupling component will give another color with the same diazo compound.

The proportions of the diazo compound to diazo coupling component are well known and do not form a part of this invention. Generally it is best to include an excess of the diazo coupling component in the treating composition to insure the presence of sufficient diazo coupling component for reaction with any of the diazo components which may be present.

The acidic materials used to adjust the pH to a level below that which permits coupling may be selected of such compounds as tartaric acid, boric acid, acetic acid, maleic acid, citric acid or inorganic salts of a weak base in a strong acid, such as ammonium sulphate, aluminum sulphate, sodium acid sulphate and the like. The amount of acid present to insure stabilization of the composition in the diazotype sheet is to some extent dependent upon the particular diazo compound. Normally suffi-

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cient acid is added when necessary to lower the pH to a point where coupling is prevented for long periods of time but not so much is used as will slow the alkalyzing process necessary to adjust the pH for coupling reaction when the imaged sheet is brought into surface contact with the developing sheet for the release of alkalyzing vapors.

As the medium for generating ammonia or other base, use may also be made of ammonium benzoate, ammonium citrate, ammonium tartarate, morpholine citrate and the like, or amines such as morpholine, diethanolamine, or polyamino compounds such as chromium hexamino compounds of the type used in Example 4.

It is desirable to make use of cellulose acetate or other cellulose ether or ester derivative such as ethyl cellulose, cellulose propionate, cellulose acetate butyrate and the like as an ingredient in the diazotype coating composition. It is believed that the cellulose derivative functions in the coating composition in combination with certain rapidly evaporating solvents of the type acetone to limit penetration of the coating into the base tissue. This causes the dye forming components to remain readily accessible in the surface of the coated sheet for immediate coupling in response to the presence of the alkalyzing vapors forced into contacting relation therewith during the reproduction process. Without such ingredients in the coating composition, conventional diazotype sheets such as the sheets of Eaton or the sheet stock used in the Ozalid or Bruning processes would be secured and copy of sufficient intensity would not result unless substantially greater amounts of the alkalyzing vapors were caused to be present for a greater length of time as is produced in the vapor generating chambers of the Ozalid process or the direct application of an alkaline solution as in the Eaton process to effect pH adjustment to cause coupling to take place. With such sheets of the prior art it would be impractical to make use of the developing sheet used in the practice of this invention for more than one cycle and even then copy of inferior quality would be produced.

The following will represent a composition embodying the preferred concept of this invention for use in the manufacture of a diazotype sheet suitable for office copy work:

Example 5

20 parts para-diazo ethyl hydroxy ethyl aniline zinc chloride
20 parts para-diazo dimethyl aniline zinc chloride
15 parts para-diazo diethyl aniline zinc chloride
25 parts resorcinol
8 parts phloroglucinol
70 parts thiourea
140 parts citric acid
70 parts phosphoric acid
30 parts boric acid
90 parts aluminum sulphate
215 parts water
900 parts acetone
45 parts cellulose acetate

The above composition is coated in weights of about 3-10 pounds per 3000 square feet of surface area onto a paper such as standard dry process diazo paper. The coating composition is dried in an air circulating oven heated to a temperature of about 150° F. or else allowed to air dry.

The coated sheet may be used in the production of copy in the manner previously described in connection

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with the sheets produced by Example 1. The cellulose acetate and the rapid evaporation of the acetone tends to limit the penetration of the coating composition into the interior of the base sheet so that the coating forms on the surface thereof where the diazo compounds and the couplers are readily available for reaction to form the dyestuff upon adjustment of the pH to the desired range for coupling.

It will be apparent from the description that a diazotype copy process is provided which is readily adaptable for office copy work in that the elements used in the preparation thereof constitute dry sheets of paper which are brought together and heated by equipment which can be made simple and readily available and which can be operated by inexperienced labor. The production of copy is immediate and capable of use without special steps such as drying or coating.

It will be understood that changes may be made in the manner of kissing the diazotype sheet with the latent image with the developing sheet and for heating same to liberate vapors for the development of copy and that changes may be made in the details of formulation as well as in the construction of the diazotype sheet and the developing sheet, without departing from the spirit of the invention, especially as defined in the following claim.

We claim:

A method for the production of copy comprising positioning a positive in surface contact with a copy sheet having a coating dried on the surface thereof formed with a composition containing a cellulose derivative selected from the group consisting of cellulose ethers and cellulose esters and acetone as the major solvent to prevent excessive penetration into the support and containing a diazo compound capable of coupling to form an azo dyestuff, a diazo coupling component and an acid medium present in sufficient amount to prevent a coupling reaction to form a dyestuff, exposing the coated support through the positive to destroy the diazo in the exposed areas leaving a latent image of the dye forming components in the unexposed areas, contacting the coated surface of the support containing the latent image with a sheet containing a chromium hexamino compound capable of releasing a base by volatilization at elevated temperature, heating the sheet during contact to cause volatilization of the base from the sheet to the coated surface of the copy sheet to adjust the pH in the coating forming the latent image whereby a coupling reaction takes place to develop the latent image on the support as an azo dyestuff.

References Cited in the file of this patent

UNITED STATES PATENTS

1,966,755	D'Hauterive	July 17, 1934
2,228,562	Dieterle	Jan. 14, 1941
2,474,700	Slifkin	June 28, 1949
2,501,874	Peterson	Mar. 28, 1950
2,603,564	Maxcy	July 15, 1952

FOREIGN PATENTS

398,671	Great Britain	Sept. 21, 1933
553,508	Great Britain	May 25, 1943

OTHER REFERENCES

Mellor: Comprehensive Treatise of Inorganic and Theoretical Chemistry, volume II, page 373, 1931. Publisher Longmans, Green and Company, New York.