July 29, 1969 V. LINOWITZKI ET AL 3,458,314

PROCESS AND DEVICE FOR DEVELOPING A TWO-COMPONENT DIAZOTYPE MATERIAL

Filed Sept. 23, 1964 2 Sheets-Sheet 1

FIG. 1

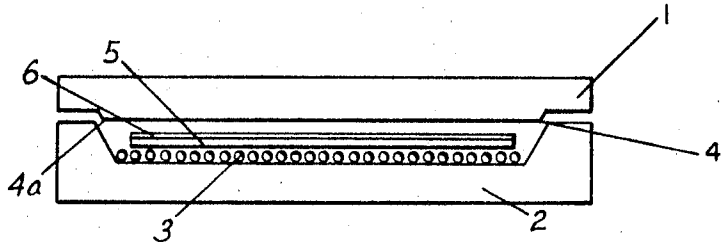

FIG. 2

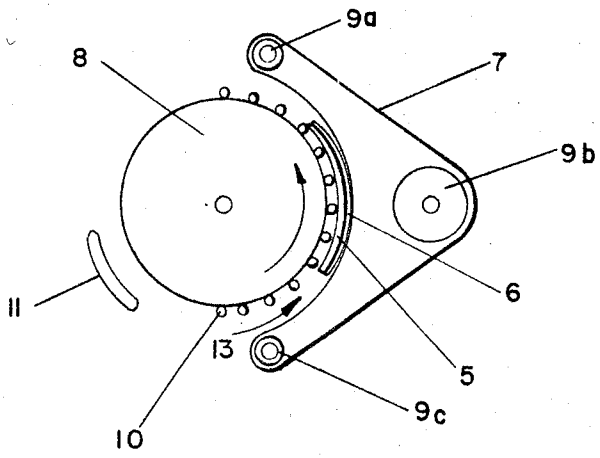

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FIG. 3

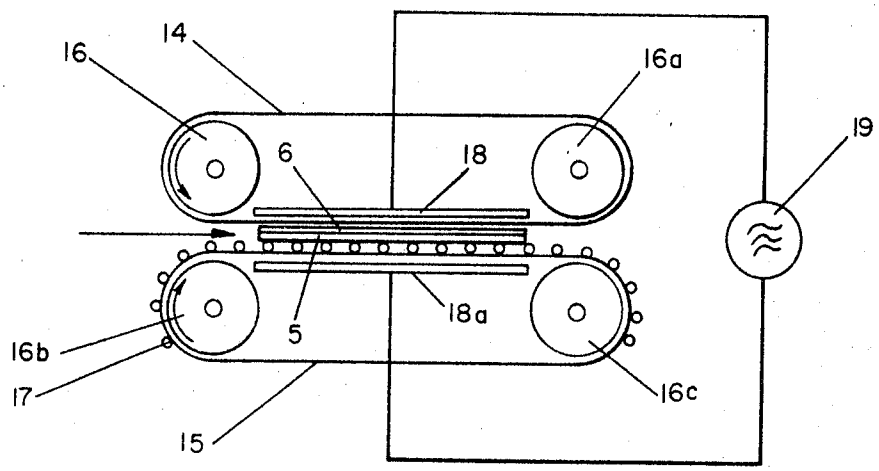
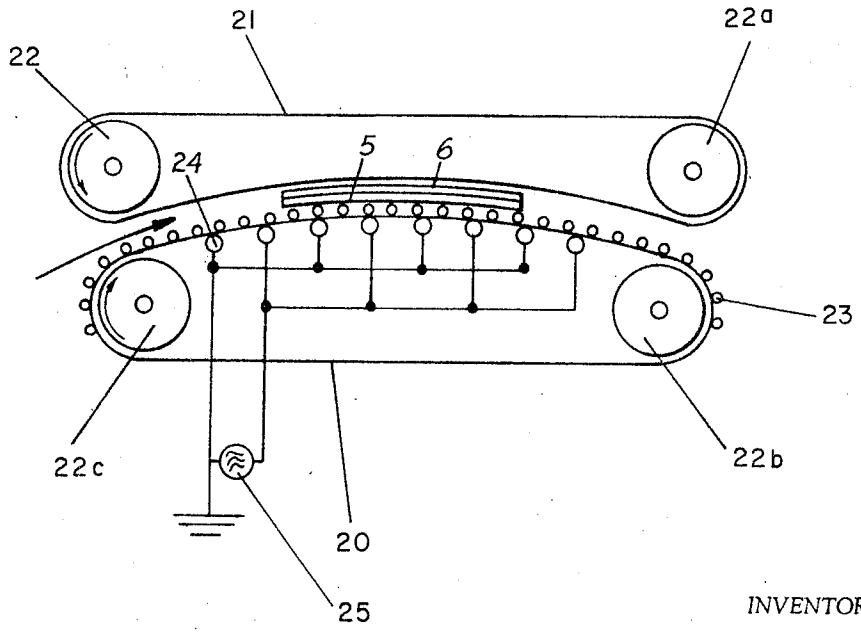


FIG. 4



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3,458,314

PROCESS AND DEVICE FOR DEVELOPING A TWO-COMPONENT DIAZOTYPE MATERIAL

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Int. Cl. G03c 1/48, 1/52
U.S. Cl. 96—49 3 Claims

The present invention relates to a process for developing a two-component diazotype copying material containing a compound that is thermally decomposable to create an alkaline environment. The invention further relates to a device for carrying out the process.

It is known that certain two-component diazotype copying materials are capable of thermal development after an imagewise exposure. In these materials either one or both sides of the sheet is exposed to heat in such a manner that much of the vapors required for creating an alkaline environment escaped from the sheet without effecting development.

In terms of efficiency, this is advantageous because a considerable amount of produced gas does not influence the diazo coating in the desired manner, but escapes unused to the surrounding air. This has the further disadvantage of producing a strong, undesirable odor in the vicinity. Furthermore, it is necessary to make up for this loss of gas by considerably increasing the gas-forming compounds in the copying material. This results in decreased shelf-life of such a material.

Devices for carrying out the above process are also known. They receive the heat diazo paper in a slot formed by two conveying elements and subject it to the influence of heat. In all cases, however, the developing temperature must be below the decomposition temperature of the heat diazo compound. At these conditions, the gas-producing material decomposes relatively slowly. This decreases the developing speed and the quality of the resulting copies. In most cases this produces an undesirable flat or dull color in the image area.

Therefore, one object of the present invention is to provide a process for obtaining a strongly-developed tone in the image areas of a thermally developable diazotype material in a relatively short developing time, with little unpleasant odor, and which at the same time improves the shelf-life of the material.

Another object is to provide a process for developing a two-component diazotype copying material containing additional compounds which thermally decompose gases which create a neutral or alkaline environment, which process is characterized by the fact that the copying material is exposed to the influence of heat in a substantially gas-tight system and that the gas or vapor produced in that way is at the same time brought to an elevated temperature on a surface which is not in contact with the copying material and which does not face the diazo coating, whereby the gas develops the coating more intensively.

Another object is to provide a device for the process, which device is characterized by two movable elements, at least one of which can be heated, whereas the other one may be cooled if desired, and the surface parts of which are in contact with each other over a large area of their surface at least during the developing process, the surface of the element to be heated being constructed in such a way that the larger part of the surface is kept at a distance

from the surface of the copying material with the aid of spacers.

Other objects will become apparent in the course of the following specification.

In the drawing:

FIGURE 1 is a side elevational view of one embodiment of the present invention;

FIGURE 2 is a side sectional view of another embodiment providing for continuous operation;

FIGURE 3 is a side sectional view of a preferred embodiment; and

FIGURE 4 is a side sectional view of another embodiment.

By means of the present invention, quick and complete development of the diazotype copying material is achieved by substantially complete utilization of the coloring component present in the coating and not destroyed by the preceding imagewise exposure. Deep colors are thus obtained. By using a gas-tight chamber or container, the best possible utilization is made of the developing gas. It is thus possible to keep the amount of gas-producing substances as low as possible. Apart from economical reasons, this is important since it considerably increases the shelf-life of the paper because the deleterious effect of the gas-producing substances on the diazo compounds during storage is reduced to a low degree. Since the amount of produced gas is kept very low because full use is made of the gas, the presence of unpleasant odors is considerably minimized.

The two-component diazotype copying material generally comprises a vapor porous support, a light-sensitive mixture of a diazo compound and a coupling component coated on one side, and a thermally decomposable developing vapor-producing compound coated on the other side of the support. The developing vapor from the thermally decomposable compound creates a neutral or alkaline environment in the light sensitive coating.

All base materials normally used in the diazotype process may be used as supports. Base materials which allow the generated gas to permeate are particularly suitable. Supports which comply well with this requirement are papers preferably weighing between 50.0 g. to 180.0 g. per square meter. Such papers are commercially available as photo copying base papers. Transparent papers may also be used for the purpose according to the present invention.

Compounds used and known for copying purposes may be used as diazo and azo components in the light-sensitive mixture. Examples of diazo compounds are:

4-dimethylamino-benzene-diazonium chloride;
4-morpholino-benzene-diazonium chloride; and
4-pyrrolidino-3-bromo-benzene-diazonium chloride.

Examples of azo components are:
2,3-dihydroxy-naphthalene-6-sulfonic acid;
2-hydroxy-benzo-triazole-(1,2);
1,3,5-resorcyl acid-diethyl amide; and
1-(N-ethylamino)-3-hydroxy-4-methyl-benzene.

The following compounds are suitable for penetrating through a support to creat a neutral or alkaline environment on the front side under the influence of heat: compounds which initially do not show a neutral or alkaline reaction and which under the influence of heat, for example by decarboxylation or fission, change into vapors which have a neutral or alkaline reaction; and substances which initially have an alkaline reaction. The following compounds are given by way of example: amides of organic, aliphatic, mono- and poly basic carboxylic acids

with straight or branch carbon chain such as acetic acid, mono-, di-, and trichloracetic acid and polymers thereof; diamides of carboxylic acids such as oxalic acid, fumaric acid and succinic acid; and amides of acids which have one or several hydroxyl groups in the aliphatic chain, such as the amides of malic acid, tartaric acid, citric acid, hydroxy acetic acid, hydroxy butyric acid, and lactic acid. The alkyl ethers of these hydroxy carboxylic acid amides, such as the amide of 2-methoxy-acetic acid are also suitable.

Other suitable substances are the mono- or poly amines of hydrocarbons with straight or branched carbon chain such as dodecylamine and stearylamine, or alicyclic amines such as hexamethylene tetramine.

By means of the present invention, it is possible to carry out the decomposition of the gas-producing substances at a temperature at which the sensitive paper and the light sensitive compound cannot be damaged. However, since it is advantageous for the gas creating the reaction environment to have a higher temperature to be effective, the gas produced according to the present invention is brought to a higher temperature after it has been produced, whereby it is capable of penetrating the paper layer of the heat diazo paper quickly, intensively and evenly. The light sensitive diazo layer is thus exposed to a sufficient amount of hot gas in very little time. Thus, a quicker and more complete development is guaranteed. An over-heating of the diazo coating above its decomposition point does not occur. An explanation for this effect may be seen in the fact that the thermal capacity of the strongly heated gas is not sufficient to cause decomposition of the light sensitive compounds to any considerable degree. Furthermore, the entire amount of the produced gas is available for the purpose according to the present invention because the entire system is closed.

The decomposition temperatures of diazo compounds are well known and lie around 100° C. Advantageously, the diazo paper is not to be heated above this point. The increase in temperature of the produced gas always takes place externally to the diazo material and is effected through contact between the generated gas and a heated surface which is located at some distance from the material to be developed. The difference between the higher temperature of the gas and the gas producing temperature may vary within wide limits. Good results are obtained if the difference of temperature lies between 10 and 200° C., preferably between 50 and 150° C., and it is particularly advantageous if the difference is between 80 and 120° C. In this connection, the temperature of the surface used for the subsequent and additional heating of the gas may far exceed the above mentioned temperatures. The temperature of the heated surfaces depends essentially on the duration of the contact between the gas and said surface, and factors such as distance of the heating surface from the coating to be developed and the absolute heat difference.

The present invention is described below with the aid of the attached drawings. These are not intended to limit the scope of the present invention.

FIGURE 1 shows a simple embodiment of the device according to the present invention. Pressure element **1** and base element **2** are arranged one on top of the other as indicated preferably only during the developing process to form a developing chamber. Through the particular shape of the two parts, a practically gas-tight enclosure is achieved by points **4** and **4***a*. At the same time the larger part of the surface of the base element **2** is kept at a distance from the copying material to be developed by means of spacers **3**. The spacers **3** form a closed grid pattern for containing the generated vapors. The diazotype material **5**, which is provided with the diazo coating to be developed on its side **6** is introduced into the device as shown. Heating is effected through the base element **2** which can be heated to a higher temperature in known manner, for example by subjecting it to the influence of heat rays from the outside.

FIGURE 2 shows a further embodiment of the device according to the present invention which produces good results. Here, the two movable elements comprise a belt **7** and a roller **8**. The belt **7** moves on the rollers **9***a*, **9***b*, and **9***c* which guide it in such a way that the surface of belt **7**, which is situated between guide rollers **9***a*–**9***c*, maintains uniform contact with the corresponding surface of roller **8**. The surface of roller **8** is designed in such a way that its outer surface is covered by spacing devices **10**. The two-component diazotype copying material **5** travels through the device with its diazo coating **6** facing the belt **7** above the spacing devices **10**.

The diameter of the above mentioned roller **8** may vary. Rollers with a diameter between three and twenty centimeters, preferably between five and ten centimeters, have proved to be very suitable. It is not important that any particular material be used for the roller or its surface. It may, for example, be metal or a plastic material, but it should be possible for the surface to be exposed to temperatures up to approximately 300° C. without being deformed. The spacing devices may be arranged in a regular pattern such as in the form of parallel lines, squares, rectangles, rhombi, or in the form of regular or irregular depressed dots. The height of the dividers may vary between fractions of a millimeter to approximately five millimeters, preferably between 0.2 to 1.0 millimeter. The surface of the spacing device **10** which comes in contact with the copying material may be round, flattened or pointed, but the depressions or cavities must be capable of substantially enclosing the produced gas when in contact with the diazo sheet. Materials which have poor heat-conducting properties have proved to be particularly useful because they prevent the larger heat content and the higher temperatures of the roller surface to be imparted to said devices. Consequently, heat-resistant types of hard rubber or corresponding plastic materials are particularly suitable. The above mentioned spacing devices may be attached to the roller surface by covering it for example with a mesh-like structure. It was also possible to produce useful spacing devices by sticking them onto the surface or by inserting them into recesses.

Heating the roller may be effected by the aid of heat rays or by bringing the roller into contact with a heated body. For this purpose an infra-red radiator **11** was mounted outside roller **8** at a spot not covered by belt **7**. Heat radiators which are arranged inside roller **8** may also be used for heating. Heating with steam or hot air may also be used.

The roller **8** may be driven by surface drive or through its shaft, but this is not necessary if the belt **7** is designed to be movable. The belt **7** should consist preferably of a more-or-less elastic, gas-tight, heat-resistant material such as Teflon. The surface which contacts the diazo material should be smooth. At least one of the rollers **9***a*, **9***b*, or **9***c* may be driven by a motor. Preferably this is roller **9***b* which is arranged at a greater distance. Preferably, the position of guide rollers **9***a* and **9***c* is chosen in such a way that the belt which is situated between them, is likewise in surface contact with the roller, and covers more than half the surface of roller **8**. A lower surface contact which should, however, not be below 10% may also be used.

The two-component diazotype copying material to be developed is introduced into the device at point **13** and gripped by the moving parts **7** and **8** which guide it to the developing section. As the sheet of the diazo copying material moves between the movable elements **7** and **8**, these press against each other with such force that the material **5** is practically contained within a closed system. On its way through the device, while traveling between guide rollers **9***a*, and **9***c*, the non-coated side of the material **5** is exposed to heat emanating from roller **8**, whereas belt **7** which is not heated has a temperature which does not decompose the diazo coating **6** in contact with its surface. The side of the copying material which faces

the roller **8** is heated to a temperature that is sufficient to thermally decompose the gas-producing compound.

The gas thus produced (mostly ammonia) has the tendency to spread in all directions. The cavities in roller **8** which are formed by the spacers **10** confine the gas until it reaches the surface of roller **8** which is free of spacers and which has been heated to a high temperature. In contact with said surface, the gas is now heated to a higher temperature, and due to its increased kinetic energy, a large amount of the gas easily diffuses through the paper base to the diazo coating to be developed. There, it very quickly produces a neutral or alkaline environment suitable for development. A quick reaction occurs between the diazo and the azo components. As a result, the compounds which were not destroyed under the influence of light are made visible very quickly and completely. The developed copy is passed on in the direction of roller *9a* where it is removed from the device. The presence of unpleasant odors from the produced gas is negligible, since only a small amount of gas is produced and practically the entire amount is used for development.

When the device is not being used to develop diazo papers, it is advantageous to displace the guide rollers *9a* and *9b* in such a way that the belt **7** is not heated by the heated roller **8**. The same effect may, of course, be achieved by decreasing the heat or switching it off.

Furthermore, means for feeding and delivering the material may be attached to the device in known manner, but they are not shown in the accompanying drawings.

FIGURE 3 shows a preferred embodiment of the present invention. Here, the two movable elements consist of two moving endless belts **14** and **15**. These belts are supported by guide rollers **16**, *16a*, *16b*, and *16c*, at least one of which is driven by a motor. The surface of one of the two belts, in this case the heatable belt **15**, is provided with spacers **17** of the shape and design described in FIGURE 2. The material of the endless belts may also be the same as described in FIGURE 2.

The copying paper **5** to be developed, is introduced into the device in the direction indicated by the arrow and with the diazo coating **6** facing upward or away from the heatable belt **15**. It is gripped and transported by the moving belt and subjected to the process according to the present invention. The heating device in this embodiment consists of two condenser plates **18** and *18a*. The two condenser plates **18** and *18a* are connected to a high-frequency generator **19**. The heating of belt **15** required for the process according to the present invention is achieved through the fact that the belt consists of a material having a very high dielectric loss factor, whereas the endless belt **14** with its smooth surface has a low dielectric loss factor. Consequently, only belt **15** is heated whereas the temperature of belt **14** is not substantially altered. Heating arrangements of this kind are known. The shape and dimensions of the condenser plates may vary. Preferably, however, they should extend over a large area approximately as shown in the attached drawing and wide enough to develop the width of the diazo sheet. Furthermore, the distance between the condenser plate and the belt surface is as small as possible. The strength of the high-frequency field is variable and is adapted to the properties of the belt material. It was found that good results were obtained with frequencies between 10–20 megacycles per second.

Furthermore, the speed of the belt and the rate at which numbers of copies are developed are also decisive in determining the heat intensity. When using this device for the process according to the present invention, the copying material to be developed is also heated in a closed system between the two moving belts **14** and **15** and is influenced under the conditions described in connection with FIGURE 2. Here as well, images with excellent covering power of the image areas are obtained in very short times such as approximately one to two seconds.

FIGURE 4 shows an embodiment which also produced very good results. Here two endless belts **20** and **21** run over driven guide rollers **22**, *22a* *22b*, and *22c*. The surfaces of the two endless belts touch over a large area, approximately between two straight lines formed by the centers of the shafts of rollers **22** and *22c* and the shafts of rollers *22a* and *22b*. In this device, heatable belt **20** is provided with spacing surface parts **23**. The diazo paper **5** to be developed is introduced into the device in the direction indicated by the arrow and passes through said device, the development taking place within a substantially closed system. The surface of belt **21** is not provided with spacing devices.

In this device, belt **20** is also heated with the aid of a high frequency field by rod electrodes **24** arranged beneath belt **20** in a convex, concave or planar pattern relative to the direction of movement of the belt **20**. These rod electrodes **24** are alternately connected as shown to a high frequency generator **25**. In this arrangement, the main field of the high frequency field is formed very advantageously parallel and within the moving belt **20**.

Thus a quick and easily controllable heating of an endless belt is achieved. The degree of heating, that is, the strength of the high frequency field is determined here by factors discussed in relation to FIGURE 3. It is advantageous to separate belts such as **21** and **20** when the device is not being used, so that the unheated belt cannot become hot through contact with the heated belt. The separation can be achieved in known manner with the aid of mechanically or electrically controlled devices which separate the shafts of rollers **22** and *22a* from the shafts of rollers *22b* and *22c*.

When the device is used for a longer period, it is advantageous to cool the belt **21** with the aid of an air current. These cooling devices may be located adjacent to the device in known manner.

It is apparent that the described examples are capable of many variations and modifications. All such variations and modifications are to be included within the scope of the present invention.

What is claimed is:

1. A process for developing a visible azo dye on a diazotype sheet material comprising a vapor-permeable support, a two-component diazotype layer, and a layer of a heat-activatable, developing-vapor-producing composition, said process comprising the steps of:

(a) providing a heated vapor impermeable surafce having a plurality of spacer elements extending therefrom and terminating in a plane spacially disposed from said surface;

(b) positioning said sheet material substantially in said plane with said heat-activatable layer in contact with said elements, whereby vapors produced by said composition under the influence of the heat from said surface are entrapped in the space between said surface and said sheet material and are further step of positioning a vapor impermeable surface and

(c) maintaining said sheet material in said position for a time sufficient to develop said dye.

2. The process according to claim **1** wherein said diazotype layer and said composition layer are disposed on opposite sides of said support.

3. The process according to claim **2** comprising the further step of positioning a vapor impermeable surface in contact with said diazotype layer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,458,314 Dated 29 July 1969

Inventor(s) Heinz Kramer and Viktor Linowitzki

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 59, delete "further step of positioning a vapor impermeable surface" and substitute --thereby further heated by contact with said surface;--

SIGNED AND
SEALED
NOV 18 1969

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents