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## PROCESS FOR DEVELOPING DIAZOTYPE PHOTO-PRINTS WITH AMMONIA GAS

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8 Claims

### ABSTRACT OF THE DISCLOSURE

This invention relates to an improvement in a process for developing photoprints on lacquered or unlacquered diazotype films or on lacquered diazotype papers, with ammonia gas, the improvement comprising exposing the photoprint, prior to the action of the ammonia, to an atmosphere containing at least one organic solvent vapor.

This invention relates to a process for developing photoprints on lacquered or unlacquered diazotype films or on lacquered diazotype papers by means of ammonia gas.

After exposure to light, two-component diazotype material containing in its light-sensitive layer, a diazonium salt and a coupling component together with stabilizers is developed in an atmosphere containing ammonia and water vapor, generally at an elevated temperature.

Development generally is performed in a combined exposure and development apparatus in which the copying material is conveyed in contact with the original around an exposure cylinder, then automatically separated from the original and subsequently passed through the development section, which is a chamber containing warm wet ammonia gas. In order to achieve smooth operation and a high copying performance, the copying material must be passed through the development section at least at the same speed as through the exposure section. Since recently, however, the exposure time could be considerably reduced by the employment of light sources rich in energy and the use of highly light-sensitive diazo compounds, a correspondingly reduced period of time may be utilized for development. However, it is practically impossible to increase the development speed by selecting rapidly coupling diazo compounds and coupling components without simultaneously impairing the storability of the unexposed material.

The described problem particularly occurs with the recently increasingly used transparent and translucent copying materials in which the light-sensitive composition is embedded in a lacquer layer of cellulose ester or the like or in the cellulose ester film parts close to the surface. In this case, the development speed is considerably reduced by the required diffusion of ammonia and water vapor into the lacquer layer. When using such transparent and translucent materials, it thus is often not possible to utilize the available copying performance of the exposure section of modern photoprinting apparatuses.

It has been tried by various measures to accelerate the development of diazotype material with ammonia, e.g. by elevating the temperature. An optimum value has been achieved in practice the exceeding of which involves other

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disadvantages. Another possibility is the forced circulation of the gas mixture by means of which only a limited increase of the development speed can be achieved. The hitherto most effective process which is particularly suitable for the development of diazotype films is the development under increased pressure as described in German patent specification No. 1,266,641. This process, however, practically can be used only for relatively small film pieces, preferably for microfilm pictures, since exerting a correspondingly increased pressure would require too high a technical expenditure in relatively large development chambers. In any case, continuous development under increased pressure can at present hardly be realized in practice.

The development speed can also be increased by increasing the ammonia partial pressure. This is done in the simplest way by taking ammonia gas from a cylinder. Normally, the ammonia gas is developed by vaporization of an aqueous concentrated ammonia solution. As described in U.S. patent specification No. 3,373,022, this development may be intensified by saturating the supply solution with nitrogen under pressure or by the addition of alcohol to the solution. The development of lacquered or unlacquered diazotype films or of lacquered diazotype papers is not disclosed here as well as an effect of the alcohol other than the increase of the ammonia concentration in the gas chamber.

The present invention provides a process by which photoprints on lacquered or unlacquered diazotype films or on lacquered diazotype papers can be developed with the use of ammonia more rapidly than has been possible hitherto.

The present invention provides a process for developing photoprints on lacquered or unlacquered diazotype film or on lacquered diazotype papers, in which, prior to the action of the ammonia, the photoprint is exposed to an atmosphere which contains the vapor of an organic solvent or of a mixture of organic solvents.

By the pretreatment in accordance with the invention, it is achieved that, in the subsequent development with ammonia gas, the azo dye image forms substantially more rapidly and achieves its full intensity. Presumably, the surface of the lacquer layer in which the light-sensitive composition is embedded is swelled by the action of the solvent vapors so that diffusion of ammonia and water vapor into this layer and reaction of the layer constituents can take place more rapidly.

In any case, treatment with solvent vapor in accordance with the invention should begin prior to the action of ammonia in order to achieve a substantial reduction of the development time. It need not be completed, however, prior to the commencement of the action of ammonia but also may be continued within that time.

It is advantageous to perform the treatment of the invention as well as development itself at an elevated temperature since then the effect is more intense and the time of action can be correspondingly reduced. The treatment temperature may range within wide limits and depends upon various factors, such as the type of the lacquer layer, the duration of treatment, the apparatus used and particularly upon the nature and the vapor pressure of the solvent. In most cases, good results are achieved at temperatures in the range from about 30 to 90° C. Temperatures in the range from 40 to 70° C. generally are preferred.

The vapor pressure of the solvent must be sufficiently high at the treatment temperature to achieve an intense and rapid effect. Therefore, solvents generally are used which, at standard conditions, boil below 200° C., preferably between 50 and 150° C.

The nature of the solvent should be attuned to the type of the lacquer layer in which the diazotype compound is contained. The solvent should swell or soften the lacquer layer under the conditions of the treatment but not render it tacky. The suitability of a solvent or solvent mixture can be determined by simple preliminary tests, e.g. by dabbing the lacquer surface with a cloth soaked therewith. In order to achieve a particularly rapid and uniform action of the mixture of ammonia and water vapor later on, those solvents have proved particularly suitable which are at least partially miscible with water. Examples of suitable solvents are: alcohols, such as methanol, ethanol, isobutanol, and n-amyl alcohol; ketones, such as acetone or butanone; esters, such as ethyl acetate, n-butyl acetate, and ethylene glycol methyl ether acetate; and ethers, such as ethylene glycol monomethyl ether and diisopropyl ether. In the case of the predominantly used lacquer layers of cellulose esters or in the case of films of cellulose esters, e.g. cellulose acetate, cellulose acetate propionate or cellulose acetate butyrate, the lower aliphatic alcohols with 1 to 5 carbon atoms have proved particularly suitable. For reasons of physiological harmlessness, ethanol and isopropanol are particularly preferred.

In many cases, it is advantageous to use mixtures of solvent vapors since, in this manner, it is possible to adjust to a desired vapor concentration or a certain dissolving or swelling action. It is also possible by suitable solvent combinations to produce mixtures which may be used for lacquer layers of different kinds. In most cases, it is also of particular advantage when the treatment atmosphere contains water vapor in addition to solvent vapors. Such vapor mixtures may be produced either from one vaporization source containing the liquid solvent mixture or from several vaporization sources for the individual components. The mixing ratio in the gas chamber, however, preferably should be so adjusted that, in the case of condensation of liquid droplets on the lacquer layer, a homogeneous liquid phase is obtained.

The solvent vapor should act from the sensitized side of the copying material; it thus advantageously acts only after exposure and separation of the original and the copying material. The treatment of the invention may be performed in a vapor chamber arranged before the development section. For reducing the duration of treatment, the solvent vapor may be blown from a slot die onto the copying material, for example. The treatment time further depends on various factors, e.g. on the temperature, the type of the lacquer layer, and the type of the solvent mixture. The necessary treatment time may vary between a few seconds and about 1 minute, depending on the conditions. It may be so adjusted by a suitable choice of the parameters that smooth operation is guaranteed in a combined continuous copying apparatus.

Suitable diazotype materials which can be developed according to the process of the invention are lacquered and unlacquered photoprinting films and lacquered photoprinting papers, e.g. cellulose acetate films, lacquered polyesters or polycarbonate films, lacquered translucent papers or lacquered opaque photoprinting papers, in which the light-sensitive composition is embedded in the lacquer layer by diffusion sensitization or, in the case of films capable of diffusion sensitization, embedded in the surface of the film.

In the case of all such diazotype materials, the speed of development with ammonia is substantially increased by the treatment in accordance with the process of the invention.

The following examples illustrate some embodiments of the process of the invention.

## EXAMPLE 1

Onto a 75 $\mu$  thick biaxially stretched and heat-set film of polyethylene terephthalate, the surface of which had been pretreated as described in German published patent application (DAS) No. 1,228,414, there was cast an about 8 $\mu$  (after drying) thick film from the following solution:

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10	Cellulose acetate propionate with a content of about 58% of propionic acid groups, 5% of acetic acid groups, and 1% of hydroxyl groups, and of an average molecular weight of 170,000	850
	Amorphous silica having an average particle size of 1 to 2 $\mu$	200
15	Precipitated silica having an average particle size of 3 to 4 $\mu$	50
	Acetone	4,850
	Methyl ethyl ketone	4,050

20 The lacquer was dried for 3 minutes at 100° C. and the layer was sensitized with a solution of the following composition:

	Citric acid	g	5.2
25	Thiourea	g	5.8
	2-hydroxy-3-naphthoic acid-( $\beta$ -amino-ethyl) amide, as the hydrochloride	g	1.5
	3-hydroxy-4-methyl-phenylurea	g	2.6
30	1-diazo-4-diethylamino-benzene, as the tetrafluoroborate	g	8.5
	Formic acid	ml	4.8
	Water	ml	30.0
	Isopropanol	ml	140.0

35 and then dried. Four samples of the photoprinting film obtained were exposed under a translucent original and then developed as follows:

Into each of four closed developer tanks as conventionally used in photoprinting, there was placed a dish, the four dishes each containing one of the following liquids:

- (1) methanol,
- (2) isopropanol,
- (3) ethanol/water (70:30 parts by volume), and
- 45 (4) 25% aqueous ammonia solution.

For the purpose of saturation with the vapors of the liquids, the tanks were left standing for 4 hours. Three of the exposed samples were placed for 15 seconds in one of the tanks 1 to 3 and then for 30 seconds in tank 4; the fourth sample was placed for only 30 seconds in tank 4. After removal from tank 4, all samples were fully exposed to a copying lamp for destroying unreacted diazo compound. Samples 1 to 3 had black lines rich in contrast, whereas sample 4 had a weak grey-brown image. Several minutes were necessary for developing a similar sample only in box 4 to achieve a contrast corresponding to that of samples 1 to 3.

## EXAMPLE 2

Translucent paper of a weight per square meter of 80 g, was coated on one side with the following solution:

65	Cellulose acetate propionate with a content of about 58% of propionic acid groups, 5% of acetic acid groups, and 1% of hydroxyl groups, and of an average molecular weight of 170,000	g	500
	Di-(2-methoxy-ethyl)phthalate	g	100
70	Methanol	ml	1,100
	Acetone	ml	4,200

The lacquer was dried for 1½ minutes at 100° C. The lacquer layer of a weight of 12 g./m.<sup>2</sup> was sensitized with the solution described in Example 1.

Three wide-necked Erlenmeyer flasks were placed into a water bath at 35° C., and each filled with one of the following liquids:

- (1) isopropanol,
- (2) ethyl acetate, and
- (3) ethylene glycol methyl ether acetate,

and provided with beaker covers. After one hour, three samples of the diazotype material obtained above were exposed in the same manner and each was placed for 10 seconds, with the layer side down, onto the opening of a flask. The samples were then passed through the development section of a combined photoprinting machine at a speed of 8 m. per minute and then fully exposed. Samples 1 and 2 (in correspondence with the above numbering) had black image parts rich in contrast on a transparent background in the part to which solvent vapor had been applied, whereas the remainder of the copies contained weak brownish-grey image parts of a substantially poorer contrast. In the case of sample 3, the difference between the part to which vapor had been applied and the other part of the copy surrounding it was substantially smaller. A central part with a contrast comparable to that of samples 1 and 2 could be obtained, however, by repeating the test in the same manner but maintaining the flask containing ethylene glycol methyl ether acetate at a temperature of 50° C.

#### EXAMPLE 3

Cellulose acetate film was coated with the following solution and dried:

Citric acid	g	2.6
Thiourea	g	6.0
2 - hydroxy - 3 - naphthoic acid - $\beta$ - hydroxy - ethyl- amide	g	1.4
3-hydroxy-4-methyl-phenylurea	g	1.75
Formic acid	g	1.2
4-diethylamino-benzene diazonium tetrafluorobor- ate	g	4.0
Water	ml	38.0
Isopropanol	ml	48.0

Three samples were taken from the diazotype material obtained and developed without exposure to light as follows: The first sample was passed three consecutive times through the development section of a commercial combined photoprinting machine adjusted to a speed of 1 m. per minute. The color density obtained was regarded as the maximum density to be achieved. The transmission density of the developed material was measured at 5 different places by means of a Kodak-Densitometer RT-230 with a green filter and the average value was determined from the values obtained. The second sample was passed once through the development section at a speed of 10 m. per minute and immediately thereafter was passed through the exposure section in order to interrupt the development operation. The density obtained was measured as above and was 75% of the maximum value. The third sample was suspended for two minutes in an exsiccator containing an atmosphere saturated with ethanol vapor at room temperature. It was then treated as the second sample. The color density obtained was 84%. The fourth sample was processed as was the third one but with the use of acetone vapor instead of ethanol. The density obtained was 93%. Prolongation of pretreat-

ment with solvent vapor to 5 minutes involved a density increase to 88% in the case of ethanol and to about 97% in the case of acetone. In this case, the surface of the film treated with acetone was slightly tacky. The tackiness could be eliminated by using for this test the solvent atmosphere which forms above a mixture of equal parts of acetone and isopropanol.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. A process for developing two-component diazotype material comprising a film or paper support having a lacquer layer thereon or an unlacquered film which has a photosensitive composition embedded in the said lacquer layer or embedded in the surface of the said unlacquered film, said composition comprising a diazonium compound, an azo coupler, and an acidic stabilizer, which process comprises the steps of (A) exposing the photosensitive material imagewise to actinic light, (B) contacting the imagewise exposed material prior to development with an atmosphere containing at least one organic solvent in vapor form which swells or softens the film base and/or the lacquer layer but does not render them tacky during this treatment step, and (C) developing said diazotype material to form a dye image by contacting said diazotype material with ammonia gas.

2. A process according to claim 1, in which the solvent vapor continues to act on the film base and/or lacquer layer during development with ammonia.

3. A process according to claim 1 in which the solvent is at least partially miscible with water.

4. A process according to claim 1, in which the solvent vapor acts at an elevated temperature.

5. A process according to claim 4, in which the solvent vapor acts at a temperature in the range of 30 to 90° C.

6. A process according to claim 1, in which the solvent has a boiling point below 200° C.

7. A process according to claim 1, in which the atmosphere contains a mixture of vapors of different solvents.

8. A process according to claim 1, in which the atmosphere additionally contains water vapor.

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