

2,695,846

DEVELOPING OF DIAZO AND AZIDE SENSITIZED COLLOIDS

John P. Mally, Glen Cove, N. Y., assignor to Powers
Chemco, Inc., Glen Cove, N. Y., a corporation of New
York

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The present invention relates to a novel and improved process for the rapid treatment with a liquid of exposed layers of rotary photogravure tissues which are sensitized with diazo or azide tanning compounds so that printing members of the highest quality may be prepared therefrom.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the steps, processes and compositions pointed out in the appended claims.

The invention consists in the novel steps, processes, compositions and improvements herein shown and described.

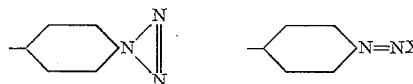
The present invention has for its object the provision of an extremely rapid and improved process for the liquid treatment of rotary photogravure tissue sensitized with a diazo or azide tanning compound or with similar organic sensitizers so that the tissue is not destroyed prior to etching of the cylinder or other printing surface. A further object is the provision of an improved process for the liquid treatment of thin sheets of gelatine or the like which have been differentially hardened in accordance with exposure to light by the tanning action of the tanning compound contained in the sheets and so that the gaseous decomposition products of the tanning compound does not impair the quality of the image on the sheet, nor does the gelatine sheet suffer any unwanted action during development or etching, such as might otherwise destroy not only the sheet of sensitized and exposed gelatine, but might necessitate the regrounding of the large and expensive copper cylinder onto which the gelatine sheet is mounted for the formation of the rotary photogravure printing member.

In accordance with the present invention, the sensitized sheet of rotary photogravure tissue comprises a sheet of thin gelatine, or other gelatinous colloid which may be selectively tanned by means of a photosensitive tanning agent, and which incorporated as the photosensitive tanning agent a diazonium or an azide tanning compound which is photosensitive, includes the —N:N— group, and on exposure to light reacts to produce a compound which renders the gelatine or gelatinous material less soluble in water or less permeable to water. Such compounds, I have found, release gaseous nitrogen on exposure to light, and if the gelatinous sheet in which they are dissolved or dispersed is immersed with water immediately after exposure to light, as is usual in rotary photogravure practice, cause the formation of relatively large blisters in the gelatinous sheet which render the gelatinous sheet unfit for further use and require that another exposed tissue be prepared, thereby delaying and increasing the cost of the operation of preparing the printing member. Such blisters may also appear during the etching process and occasionally cause the gelatinous sheet to become detached from the surface of the printing cylinder in localized areas, thereby destroying the ability of the sheet to control the penetration of the etching solution through the sheet and the localized action of the etching solution of the copper metal of which the printing surface is composed. In this connection, it must be remembered that the perfection of the resulting printing member depends entirely upon the localized action of the mordant on minute areas, each of which is almost always less than 0.01" on each side forming the square area.

The tissues for use in the process of the present inven-

tion preferably comprise a sheet of gelatinous material, such as gelatine, from about 0.001 to 0.003" in thickness, and usually containing a relatively dark finely divided pigment, which is usually of a brown, dark red or other dark color, and is sensitized with one or more of the photosensitive dyes which can exert a tanning action on the gelatinous material as these tanning compounds are decomposed, so that the exposed areas of the gelatinous material become less soluble or swell less when wet with water during the development process, and are less permeable to the mordant.

Many such tanning compounds exist, and some of them are disclosed in the patent to Zahn, No. 2,100,063 granted November 23, 1937, and in general these tanning compounds include one or the other of the following organic groups:



As will be noticed, either group includes the structure —N:N— , and either of these groups of the entire tanning compound molecule decomposes on exposure to light to liberate gaseous nitrogen.

In the first formula above, it will be noted that there are three nitrogen atoms and these are released on exposure to light, and probably replaced by an —OH group.

In the second formula, where X shows the presence of a monovalent atom such as chlorine, only two nitrogen atoms are released on exposure to light, and the group is likewise probably replaced by an —OH group. It will be understood that only a portion of the formula of the tanning compounds has been shown above, as the remainder of the molecule may vary widely, but the gelatine-tanning compounds referred to include one or the other of the above structures and include the —N:N— linkage. Such tanning compounds are generally referred to as diazo compounds, and others are referred to as azide tanning compounds.

In the conventional process of the prior art, such a layer of a gelatinous material and a suitable proportion of the tanning compound referred to is exposed to a positive image of the subject to be reproduced, is then exposed to a rotary photogravure screen, after which the gelatinous layer, usually supported on a layer of paper, is firmly pressed against the surface of the cylinder, as by rolling, and is wet with water only at the time of contact with the cylinder, the water usually being applied to the space between the gelatine and cylinder as the gelatine sheet is progressively rolled onto the cylinder. The sheet is thus securely adhered to the polished and clean surface of the copper cylinder or other printing member, the back of the paper sheet is wet with water, or with denatured alcohol and then water, and the paper layer is removed, after which the gelatine layer is developed, preparing it for application of mordant. Ferric chloride solutions are exemplary of the mordants usually used and the function of the differentially hardened layer of gelatine is to regulate the diffusion of this mordant towards the surface of the copper cylinder, thereby controlling the etching of the cylinder in accordance with the exposure which has been received by the gelatine sheet. After the etching is complete, the remainder of the gelatine sheet may be stripped from the surface of the printing member by application of an alkaline solution to the gelatine.

Due to the compact nature of the gelatine layer and its relatively strong nature prior to its being wetted with water in the development of the layer, all of the nitrogen gas released during the exposure of the sensitized gelatine sheet is retained in the sheet, and as soon as the sheet is wetted during development, the nitrogen causes blisters to appear in the sheet, due to the swollen, weakened condition of the gelatine. These blisters completely destroy the usefulness of the sheet as a diffusion controlling layer for the etching process, and often times several such sheets must be prepared before one is obtained which will produce a satisfactory printing member.

It has previously been found that these disadvantages may be overcome in actual practice by subjecting the

3

exposed sheets of sensitized gelatine prior to development to a relatively intensely reduced air pressure for a period of a half hour or longer, thereby causing the nitrogen gas to diffuse through the layer of the gelatine prior to development, and enabling the sheets of exposed gelatine to be developed in the usual manner, applied to the surface of the cylinder to be etched, and then etched in the conventional manner. However, this prior process requires the use of large and cumbersome equipment which is relatively costly and requires a considerable period of time to carry out the process sufficiently to insure that the occluded gas is fully removed from the sheet. The present invention is advantageous in that it is carried out with a minimum of apparatus, requires no prolonged treatment of the gelatine sheet and proceeds almost at once to the complete release of the occluded nitrogen.

According to the present invention, I have found that these difficulties can be easily overcome and that the formation of blisters can be consistently avoided with the resultant consistent production of uniformly good rotary photogravure printing members by treating the surface of the exposed gelatine sheet sensitized with the tanning compounds referred to a bath of relatively pure methanol, or less desirably ethanol, which may be applied by bathing, swabbing or by pouring the alcohol over the surface of the sheet of sensitized and exposed gelatine.

The methanol or ethanol used is preferably relatively pure, and under the best procedure, I prefer to use a substantially anhydrous methanol containing at least 98% or more of alcohol, but less desirably I find that it is satisfactory to wet the surface of the sensitized and exposed gelatine for one or more minutes with methanol or ethanol which is purer than about 90%, alcohol, the remainder being principally water. Such a liquid may be used time and again although it is preferable merely to wet the surface of the gelatine with the monohydric alcohol and allow it to evaporate. If a bath of the alcohol is used it finally becomes contaminated, after repeated use, with moisture from the air and with tanning compound picked up from the surface of the gelatine sheets treated so that it should be discarded as soon as contamination is apparent.

Methanol is highly preferred among the monohydric alcohols in its desirable properties in this respect. Ethanol, pure and substantially anhydrous, may be used, less desirably, but does not exhibit the rapidity nor the completeness of the action of methanol, while the propyl alcohols are substantially without effect. Thus, the invention comprises treatment with methanol or ethanol.

After treatment with methanol for a period of only one or two minutes, or with ethanol for a longer period, any

4

excess alcohol is drained from the surface of the sheet and the sheet is allowed to dry (which occurs rapidly) after which it may be applied in the conventional way to the surface of the cylinder to be etched. The backing paper is then removed, the gelatine is developed and the cylinder may then be etched as usual with no danger of blisters forming, or of the sheet becoming detached from the cylinder as the etching is in progress.

Alternatively, and less desirably, the sheet may be dipped in or bathed with methanol or ethanol, drained, and dried, but the wiping of the exposed surface of the sheet with methanol of at least 98% purity is greatly preferred.

The invention in its broader aspects is not limited to the specific steps, processes and compositions shown and described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. In the process of developing with water an exposed sheet of colloidal substance capable of being tanned sensitized with a tanning compound containing the —N:N— group which is decomposed on exposure to light to release nitrogen gas, the step of subjecting the exposed sheet to a surface treatment with a relatively pure monohydric alcohol selected from the group consisting of methanol and ethanol, prior to the wetting of the sheet with water.

2. A process as claimed in claim 1 in which the monohydric alcohol is methanol.

3. A process as claimed in claim 2 in which the alcohol is applied to the exposed surface only of the sheet.

4. In the process of developing with water an exposed sheet of colloidal substance capable of being tanned sensitized with a tanning compound containing the —N:N— group which is decomposed on exposure to light to release gas, the step of wetting the surface of the exposed, sensitized sheet with a monohydric alcohol selected from the group comprising methanol and ethanol which is at least about 90% pure, prior to the wetting of the sheet with water.

5. A process as claimed in claim 4 in which the alcohol is methanol.

6. A process as claimed in claim 5 in which the alcohol is applied to the exposed surface only of the sheet.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,100,063	Zahn	Nov. 23, 1937