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PROCESS FOR PREPARING A PLANOGRAPHIC PLATE

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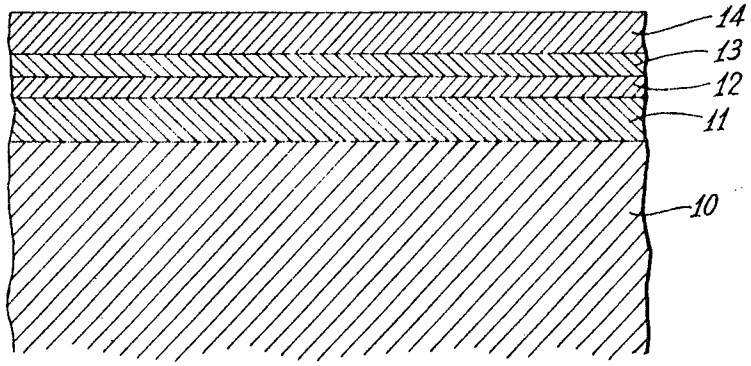


Fig. 1.

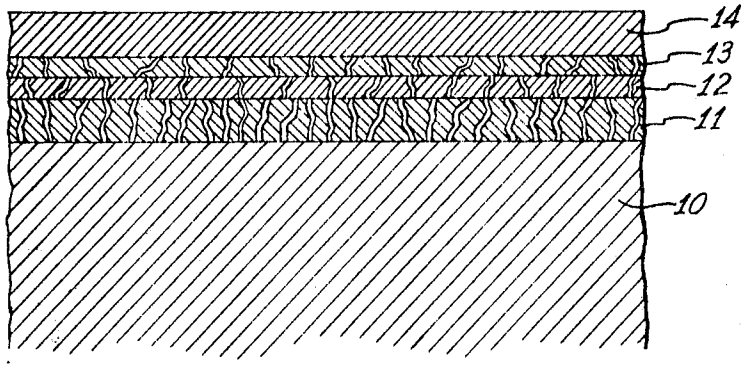


Fig. 2.

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PROCESS FOR PREPARING A PLANOGRAPHIC PLATE

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This invention refers to the printing art and, more particularly, to improved multi-metal planographic printing plates and methods of manufacture thereof.

It is well know that in accordance with the traditional principle of the lithographic art, it was considered necessary to provide, in metal plates to be used in substitution of the porous stone used in ancient times, grained or irregular metal surfaces to provide for at least a superficial porosity which might enable the otherwise non-absorbing surfaces of metal plates, to become highly absorbent and retentive surfaces either for ink or for water, in order to provide printing areas on those places where the plate is avid for greasy materials, such as printers' ink, as well as non-printing areas on those places where the metal plate is water absorbing, to place a layer of water which would avoid the adherence of the ink on said surfaces.

After long time, the essential criterion invariably followed in the printing art in the sense of graining or otherwise providing the metal plates with a certain type of porosity was abandoned since it was discovered that with use of lithographic pairs of metals, one of them was ink repellent while the other was ink absorbing and water repellent. In the interest of providing a higher fidelity of printing, smooth plates have been suggested which provide for higher fidelity and a better half-tone reproduction.

However, even when the performance of smooth plates was considered as highly satisfactory, these plates generally had the serious disadvantages of being rather brittle and of still being porous in the sense of containing intercommunicating channels and microscopic holes which allow the passage of vapors, fumes or liquids from one face to the other face of each metal layer, thus creating a shadow effect after a relatively short number of printing runs, this shadow effect rendering the plate useless after a few printing runs.

It is believed that the shadowing effect of the metal plates is due to the fact that the capillarity effect provided by the porosity of the metal layers permits the passage of at least some fumes of the several acid reactants used in the printing operation and in the development of the lithographic plates for use thereof in a printing operation, thereby allowing these fumes or vapors to act on the base metal which is commonly a chemically non-resistant metal, thus creating some corrosion effect which, as the layers are very thin and porous, reflects back toward the surface of the working metals, thereby influencing the ink absorbing properties of one of said metals and the ink repelling, water absorbing properties of the other metal. Thus, when these plates are used for multi-color printing, it may happen that an image area of one of the plates corresponds to a non-image area of another, with the ink already deposited influencing the latter, thereby spoiling the printed material obtained if this printed material is supposed to be of a high quality.

Besides the shadowing effect above described, there are other disadvantages created by porosity in the printing art, all of which adds up to provide for the spoilage of a printing plate in a relatively short time, especially if these plates are intended for use in printing operations to obtain a high quality printed material.

It has been suggested to provide a multi-metallic planographic plate having layers deposited under very tight controls in order to obtain practically non-porous layers in order to overcome all the above defects.

While the plates produced in accordance with this principle of providing practically non-porous layers of metals work in a very satisfactory manner, it is quite apparent that the cost of producing said plates may be considerably increased by the tight control which must be exerted on the deposition operations in order to obtain a constant quality on each metal layer which may provide for the practical absence of porosity in each of the working layers.

On the other hand, the metal layers applied on a metal base as practically non-porous layers must be built up to a considerable thickness in order to avoid as much as possible the existance of any porosity, in order to achieve the goal of avoiding the influence of the external agents on the base metal and the influence of the thus corroded base metal toward the working layers. This fact, and the fact that the layers in order to be non-porous must also be generally provided with very small crystals which are highly packaged, generally results in plates which are liable to become cracked at least on the outer chromium layer after some time, more particularly, when these plates are bent in order to adapt them to be handled by the cylinder of a printing machine.

On the other hand, it has been also suggested that a planographic plate which will overcome the aforementioned difficulties and still provide a very high fidelity, must be a bright plate, that is, must be a plate comprising copper and chromium layers of a very smooth bright surface in order to reproduce a very fine dot structure such as 300 or more lines for fine work. This type of bright copper layers, however, have a very different coefficient of expansion as compared to the chromium deposited thereon, so that the pair of working layers is subjected to great differential stresses and are sometimes cracked in use, thus precluding its efficient performance.

On the other hand, a bright surface on the printing plate is also disadvantagous due to the fact that the operator of the printing machine is generally unable to distinguish moist surfaces from dry surfaces on the non-image areas, to check if the plate is working right.

On the other hand, while a matte copper layer also provided with fine densely packed crystals has a coefficient of expansion more like that of the chromium layer and generally avoids any cracking thereof, and while the matte finish provides for the clear distinction between moist and dry surfaces thus allowing a close visual control on the part of the operator, these matte layers are unable to reproduce a fine dot structure to the extent the bright layers do. This fact is a very important reason why it is sometimes preferred to produce bright plates in spite of the also important drawbacks shown thereby.

In order to solve the cracking problem especially on the chromium layer, it has been necessary to apply very

thin chromium coatings with the consequent reduction in the effective life of the plates. This solution, therefore, cannot be considered as a very good one, since the cracking tendency of a plate is avoided only at the expense of adversely effecting other properties thereof.

Having in mind the defects of the prior art planographic plates, it is the primary object of the present invention to provide a printing plate that will overcome and/or substantially eliminate all the aforementioned defects and disadvantages and still produce images with high fidelity, with increased wearability and useful life, which will enable an increase of press speed and operation, reduce water and ink consumption, greatly reduce press stoppage and completely eliminate the tendency toward the formation of cracks in the different metal layers even when subjected to extreme conditions.

Another object of the invention is to provide a method for producing planographic printing plates having the foregoing advantages and characteristics.

A still further object of the invention is to provide a planographic printing plate which will have a surface appearance such that will allow the clear distinction between the image and the non-image areas, as well as between moist and dry surfaces on the non-image areas.

An additional object of the invention is to provide a printing plate of the above character, additionally comprising a metal layer suitable to provide for the amendability of the plate after development and etching.

Another and additional object is to provide a printing plate having ability for being used in lithographic equipment and also in direct printing with a long life and high efficiency.

The novel features that are considered characteristic of the invention are set forth with particularity in the appended claims. The invention itself, however, both as to its organization and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings, wherein like reference characters indicate similar parts throughout the several figures and in which:

FIG. 1 is an enlarged fragmentary cross-sectional diagrammatic view taken through a plate manufactured in accordance with one embodiment of the invention; and

FIG. 2 is an enlarged fragmentary cross-sectional diagrammatic view of the plate illustrated in FIG. 1, but showing in an exaggerated manner the porosity through each one of the layers and the interruption of direct channels from the base to the outer working layers.

Broadly speaking, the present invention is based on the provision of a metal or non-metal base **10** suitably prepared for the reception of a sublayer **11** of alkaline copper or nickel, which sublayer will act as an insulation between the material of the base and the working metals. The working metals are applied in the form of a composite acid copper layer **12, 13**, and a finishing chromium layer **14**, and may also comprise an underlaying chromium layer (not shown) to enable amendment of the plate and a nickel layer (not shown) between this underlaying chromium layer and the acid copper layer **12, 13**.

More particularly, the working layers of the plate in accordance with a second embodiment of the present invention can comprise over the alkaline copper of nickel sublayer **11**, a layer of chromium having a high hardness, smoothness and practical absence of grain, in order to act as a base for the subsequent working layers. Next to the first chromium layer, the plate in accordance with this embodiment comprises a nickel shot to provide for the suitable bonding of the copper layer **12, 13** the latter being comprised of a bright acid copper layer **12** followed by a matte acid copper layer **13** in order to form a composite acid copper layer which forms one of the essential characteristics of the plate of the present invention. Finally, the planographic plate of the present invention comprises a finishing chromium layer **14** having a highly smooth, non-porous, non-grained surface and being of a considerable hardness to provide a high resistance to marring and mistreatment in general, as well as to the normal use and abrasion caused by the inking rolls.

As the surface of the plate built in accordance with the present invention is quite smooth and graining or any other type of cavities are completely absent, the photosensitive layer which will be applied for its development will be provided with an essentially uniform thickness which obviously will avoid light refractions and the printing dots will be faithfully reproduced from the transparency used for its preparation. As the chromium layer of the plate of the instant invention is also provided with a nearly perfect uniform thickness, there is no possibility for the etching bath to dig toward the sides leaving weak edges on the dots, and therefore a plate is produced which dots will always be quite neat and faithful as compared to the original and for quite an extended life.

Briefly, the present invention resides in the discovery that the base metal can be isolated from the working metals not only by having a plurality of sublayers and working layers formed as practically non-porous layers but, on the contrary, by superposing at least two layers having different types of porosities in order to break the capillarity and avoid the passage of fumes or other types of fluids from the base **10** to the working layers and back toward the base. On the other hand, one of the most important features of the present invention resides in the application of an electroplated composite layer of bright acid copper **12** and matte acid copper **13** to give the plate a higher flexibility and to avoid the tendency toward cracking possessed by the non-porous plates of the prior art.

As shown in FIG. 2 which is a diagrammatic view of the profile of the plate showing the several layers arranged on the base **10**, each one of the layers **11, 12, 13** and **14** may have a plurality of pores which are illustrated in the form of small ducts communicating the two faces of each plate and providing passages for fumes or other fluids from one side of each layer to the other.

It is well known that a sublayer such as **11**, either comprising alkaline copper or nickel, is generally materially porous and while providing an anchorage layer for the acid copper layer **12**, it does not in itself provide an insulating layer strictly speaking. Each of the pores diagrammatically shown through layer **11** can conduct fumes or other fluids from the upper surface of layer **11** to the intersurface thereof with base **10**, thus corroding the base and allowing some influence of this corrosion to reflect back toward the surface, thereby adversely affecting the performance of the upper layers. However, as clearly shown in FIG. 2, the first low porosity acid copper layer **12**, of a bright character, has quite fewer pores and still fewer pores directly connected with pores of layer **11**. The lack of matching of the pores from one layer to the next practically isolates the working layers avoiding any influence of the fluids evolved by the treating chemicals to go toward the surface of the base **10**, therefore providing a nearly perfectly insulated base **10** which is very seldom connected by pores to the working layers. Should this layer **12** of bright acid copper constitute the first working layer, according to the probability principles, some pores could still be expected to be directly connected with the base **10** thus influencing the first or ink retaining working surfaces. However, in the plate built in accordance with the present invention, a second acid copper layer **13** is provided in order to form the composite acid copper layer. The acid copper layer **13** is a matte copper layer which is also of very low porosity, with just a few pores passing from one face to the other thereof. These randomly distributed pores could be expected to match with pores of layer **12** with a very small probability and furthermore, the probability that one of these pores be simultaneously connected with one of the pores of layer **12** and one of the pores of layer **11**

is negligible, so that the surface of the matte acid copper layer **13** can be considered as perfectly and absolutely insulated from the base **10**, thus providing a working layer completely isolated from the influence of the base and therefore avoiding any shadowing effect of the type mentioned above.

The chromium working layer **14**, therefore, will form a lithographic pair with the matte acid copper **13**, thereby providing a lithographic plate which, while not having layers strictly non-porous, will work with the same or with a higher efficiency as a lithographic plate comprising difficultly obtainable non-porous layers.

In view of the above, the plate of the present invention can be manufactured at a substantially lower cost than a plate having non-porous layers, and will produce the same or even better and more uniform results than the latter. The only layer which must be preferably practically non-porous is the chromium layer **14** in order to produce a suitable lithographic plate for very long printing runs.

If the plate in accordance with the present invention is intended to be an amendable plate, a chromium layer (not shown) is electroplated between the sublayer **11** and the first copper layer **12**, followed by a nickel shot (not shown) which receives the first acid copper layer **12** thereon. This plate will work under the same principles as the basic plate described in the above, with the only difference that, if an amendment is desired, an area of the composite copper layer can be eliminated by applying a solvent therefor in order to uncover the underlaying chromium layer to provide for a lithographic pair which, while not with the same quality as the outer lithographic plate, can serve to provide the plate of the present invention with an amendable characteristic.

Briefly, the preferred process of the present invention comprises the steps of first applying, on a suitably prepared base, either metallic or non-metallic, a sublayer suitable for providing for the reception of the working layers, and then the said working layers are applied, viz, first a copper layer deposited from an electrolytic acid bath and in the presence of a crystal growth reducing agent which in this case is a commercial brightener, then a second copper layer electroplated from an acid bath and in the presence of a double metal salt such as aluminum potassium sulfate in order to provide a matte acid copper layer and finally, a chromium layer is deposited under conditions such that a very high hardness and a sufficient flexibility are obtained, to avoid cracking when the plate is bent to place it on the roll of a printing machine, which non-cracking property is remarkably improved because of the composite layer of bright acid cooper and matte acid copper.

If desired, on the sublayer applied to the base, there is deposited a chromium layer to enable this plate to be amended as above described, which chromium layer is deposited by the same process as the finishing chromium layer but using a shorter time since in this particular case a considerable thickness is not necessary. On this chromium layer, a very thin nickel layer is applied, in order to provide for the good adhesion of the overlaying working layers.

According to one embodiment of the present invention, reference will be had to a multi-metallic plate wherein a ferrous steel sheet is used as a base. This base is polished, washed, degreased preferably in an electrolytic bath, again washed with water, pickled preferably in a sulfuric acid dipping bath with a concentration of about 10% and again washed with water to remove the acid.

When the sublayer to be used in the plate of the present invention is alkaline copper, it is generally necessary to carry out a neutralization step after the last washing step, which neutralization can be effected by dipping the plate in a caustic soda or sodium cyanide bath at approximately 10% concentrations for about 30 seconds in order to completely remove the pickling acid.

The alkaline copper plating step is then performed in an electrolytic bath comprising from 30 to 60 grams per liter of copper cyanide, from 10 to 25 grams per liter of an alkaline cyanide such as sodium cyanide and from 10 to 35 grams per liter of a caustic alkali such as sodium hydroxide, as well as from 20 to 40 grams per liter of sodium potassium tartrate. This alkaline copper layer will serve as a base for the following working layer of the present invention. In order to effect the alkaline copper plating step of the process, it is preferred to use a bath temperature of about 50 to 60° C. and the plate to be treated is connected as a cathode, applying a current density of from 1 to 3 amperes per square decimeter for a period of from about 2 to 10 minutes, preferably 5 minutes and stirring the bath by a mechanical apparatus in the vat.

In accordance with an ancillary feature of the present invention, the sublayer applied for the reception of the working layers is a nickel layer which can be bright or matte. Said nickel sublayer is applied from a bath comprising, in accordance with the particularly preferred embodiment of the invention, a total nickel sulfate content of from 20 to 30 grams per liter and a total nickel chloride content of from 40 to 50 grams per liter. A current density of from 2 to 4, preferably 3 amperes per square decimeter is used at a bath temperature comprised between room temperature and 56° C., preferably 40° C., although temperatures above or below that range are also useful, and a pH of from 5 to 6, preferably 5.5. The residence time of the plate within the nickel plating bath is of about 5 minutes. If a bright nickel layer is required, a conventional brightener will be added to the above described nickel plating bath. Also, in this particular case it is necessary to stir the solution, generally by blowing air into the nickel plating bath, which is continuously filtered by recirculation in order to maintain it absolutely clean.

In the case of depositing nickel as a sublayer in the plate of the present invention, it will be obvious that the neutralization step will not be required, since the nickel plating bath is acid and does not require the removal of the pickling acid.

After thus preparing the base sheet by the deposition of the sublayer, the working metal layers of the planographic plate are deposited, said working metal layers comprising, in accordance with one embodiment of the invention, the above described composite acid copper layer and a finishing chromium layer, or in accordance with another embodiment of the invention, a first chrominum layer for enabling the plate to be amended, followed by a very thin nickel layer and then the composite acid copper layer and the chromium finishing layer. The process of the invention will be described in terms of this second embodiment of the invention, but it must be understood that the underlaying chromium and nickel layers can be removed from the plate without however departing from the scope and spirit of the invention.

In accordance with the illustrative embodiment of the invention, after preparing the plate in the above mentioned manner, a first chromium layer is applied to act as a base to enable the planographic plate of the invention to be amended by the removal of the copper layer above, this chromium layer being commonly deposited in a bath comprising chromic acid in the presence of sulfuric acid, the chromium plating operation being preferably carried out at a temperature of from 35 to 50° C., preferably 40° C., under a current density of about 15 to 22 amperes per square decimeter, preferably 20 amperes per square decimeter and for a period of not more than 5 minutes in order to provide a relatively thin chromium layer as a base for the amending of the plate of the present invention.

The chromium bath is recovered by dipping the plate in water and then the plate is spray-washed with water in order to prepare it for the reception of a thin nickel

layer on the chromium, which nickel layer can be deposited by the same process as above described for the nickel sublayer in accordance with one of the embodiments of the invention. The nickel bath is also recovered by dipping the plate in water, and the plate is spray-washed with water to prepare it for the reception of the first bright acid copper layer, which is deposited in accordance with the process next to be described.

On the nickel layer thus deposited, a composite acid copper layer is then applied by first depositing a bright acid copper layer through the use of an acid copper bath which comprises a solution of from 150 to 250 grams per liter of a suitable copper salt such as the sulfate and from 40 to 70 grams per liter of sulfuric acid, in the presence of a brightener, and stirring the bath by blowing air through the bottom of the vat to obtain uniformity of composition. In this operation, the temperature is maintained under 35° C. when the brightener used is of the organic type, and preferably between 21 and 32° C., since at a higher temperature said agent tends to decompose, thereby precluding the good performance of this acid copper plating bath. In the bright acid copper plating operation, the plate acts as a cathode and a current density 2.5 to 3.5, preferably 3 amperes per square decimeter is applied for a period of time of about 5 to 10 minutes, preferably 5 minutes.

Next to the bright acid copper layer, a matte acid copper layer is deposited preferably introducing an intermediate water washing step in order to remove the bright acid copper bath previously used.

For this purpose, the plate is introduced in a bath comprising a solution of 150 to 250 grams per liter of copper sulfate and from 40 to 70 grams per liter of sulfuric acid in the absence of any brightener and, instead, in the presence of an amount of about 30 to 50 grams per liter of a double metal salt such as aluminum potassium sulfate. The bath is stirred by air blown through the bottom of the vat to obtain uniformity of composition, and a current density of from 2.5 to 3.5, preferably 3 amperes per square decimeter is used for a period of time of about 5 to 15 minutes, preferably 5 minutes, and at a temperature of from 15° C. to the boiling point of the bath, preferably 30° C.

Then the plate is again washed with water, and a finishing hard chromium layer is applied, this operation being effected by connecting the plate to the cathode of a vat containing a bath comprising from 250 to 350 grams per liter of chromic acid in the presence of from 2.5 to 3.5 grams per liter of sulfuric acid, the chrome plating operation being preferably carried out at a temperature of from 35 to 50° C., preferably 40° C., under a current density of about 14 to 26 amperes, preferably 22 amperes per square decimeter, and for a period of from 10 to 25 minutes, preferably 15 minutes. Finally, the chromium bath is recovered by dipping the plate in water and the finished plate is washed with water.

While in the above a ferrous base has been used to illustrate the process for the obtention of the novel planographic printing plates of the invention, this process is equally applicable to any other type of base sheet, either metallic or non-metallic. For instance, an aluminum sheet can be used, which may be degreased, washed with water, again degreased, again washed, pickled with acid, again washed and subjected to a zinc plating operation to leave it ready, after a final washing operation, for the reception of an alkaline copper sublayer and for subjecting the same to the sequence of operations described in the above.

It has been shown that the plate of the present invention, which comprises a composite acid copper layer, produces images with a very high fidelity, at least equivalent to those produced by planographic printing plates comprising practically non-porous metal layers, without the need of a very tight control for the deposition of the layers, since in this particular case said layers must not necessarily be practically non-porous. The capillarity-breaking effect of the plurality of layers accounts for the absence of any influence from the base toward the working surfaces and back toward the base and, what is more important, this composite acid copper layer provides the plate with a complete absence of tendency to cracking even when subjected to very drastic conditions.

On the other hand, the plates of the present invention possess distinctive advantages as compared to the prior art plates because, while providing a remarkable printing fidelity and a complete absence of cracking tendency in the finishing layer, they also render the image areas easily distinguishable from the non-image areas and the moist surfaces clearly distinguishable from the dry surfaces on the non-image areas and finally they permit the application of a much harder and thicker chromium finishing layer in view of the fact that the tendency to cracking has been completely eliminated and an unusual and unexpected flexibility has been provided to the whole structure of metal layers on the base.

In accordance with the embodiment of the invention which comprises an underlying chromium layer, any one skilled in the art will clearly see that, with the plate built with this chromium layer, said plate can be easily amended, in order to eliminate a printing area which is not desired, by the manual or mechanical application of an acid solution in order to completely remove the copper layers on those places where said copper layers are providing an image area, to thereby expose the underlaying chromium layer which will act as an ink-repellent layer in the same manner as the finishing chromium layer, thereby providing an amended plate which can be used for another printing operation wherein certain portions of the first printing operation have been removed.

Although certain specific embodiments of the invention have been shown and described, it is obvious that many modifications thereof are possible. The invention, therefore, is not to be restricted except insofar as is necessitated by the prior art and by the spirit of the appended claims.

That which is claimed as new is:

1. Process for producing a printing plate, comprising preparing a printing plate base sheet for electroplating, electroplating on at least one side thereof a copper ink adhering layer from an acid bath containing a brightener; electroplating on said copper layer another copper ink adhering layer from an acid bath containing a double metal salt to produce a matte acid copper layer; and electroplating on said copper layer a layer of hard non-porous chromium.

2. Process for producing a printing plate comprising preparing a printing plate base sheet for electroplating, electroplating on at least one side thereof a metal sublayer; electroplating on said sublayer a copper ink adhering layer from an acid bath containing a brightener; electroplating on said copper layer another copper ink adhering layer from an acid bath containing a double metal salt to produce a matte acid copper layer; and electroplating on said copper layer a layer of hard non-porous chromium.

3. Process for producing a printing plate according to claim 2, wherein said sublayer is a copper layer plated from an alkaline bath.

4. Process for producing a printing plate according to claim 2, wherein said sublayer is a nickel layer plated from an acid bath.

5. Process for producing a printing plate comprising preparing a printing plate base sheet for electroplating, electroplating on at least one side thereof a metal sublayer; electroplating on said sublayer a first non-grained smooth chromium layer; electroplating a thin nickel layer on said first chromium layer; electroplating on said nickel layer a copper ink adhering layer from an acid bath containing a brightener; electroplating on said copper layer another copper ink adhering layer from an acid bath containing

a double metal salt; and electroplating on said copper layer a layer of hard non-porous chromium.

References Cited

UNITED STATES PATENTS

2,678,909	5/1954	Jernstedt et al.	204—41
3,280,736	10/1966	Schafler et al.	101—459
3,282,659	11/1966	Harrouer	204—40

FOREIGN PATENTS

632,377 12/1961 Canada.

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U.S. Cl. X.R.

101—459; 204—17