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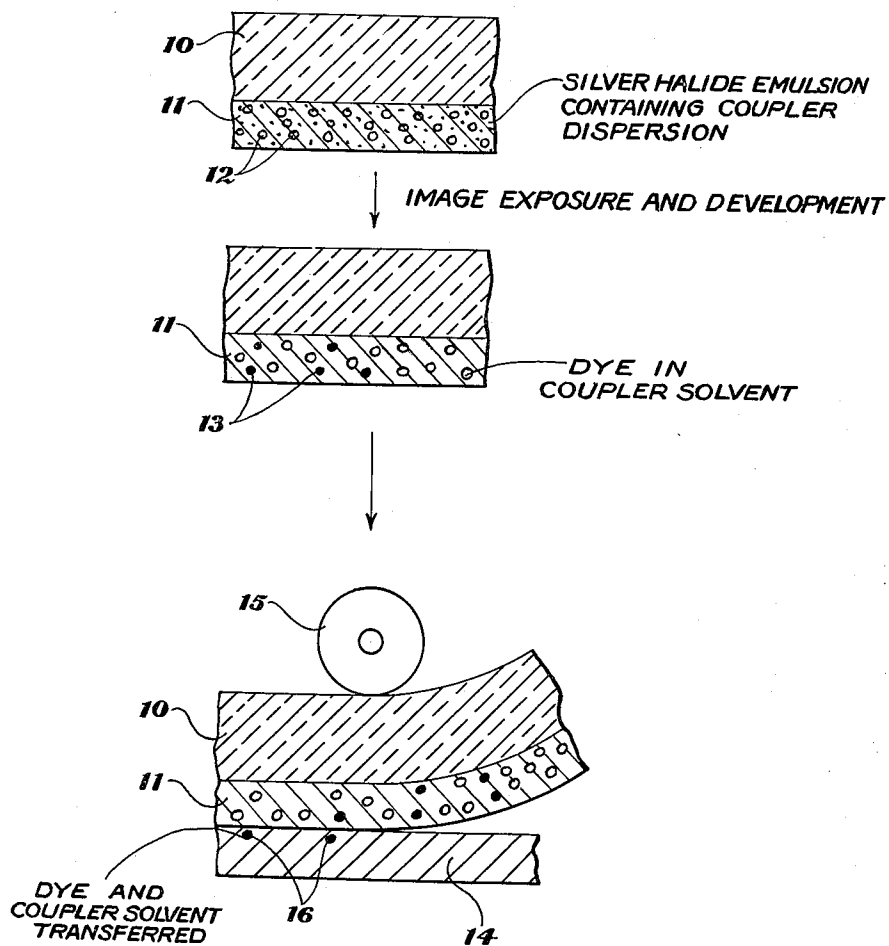
T. I. ABBOTT ET AL
PRESSURE IMAGE TRANSFER PROCESS

3,012,885

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2 Sheets-Sheet 1

Fig. 1



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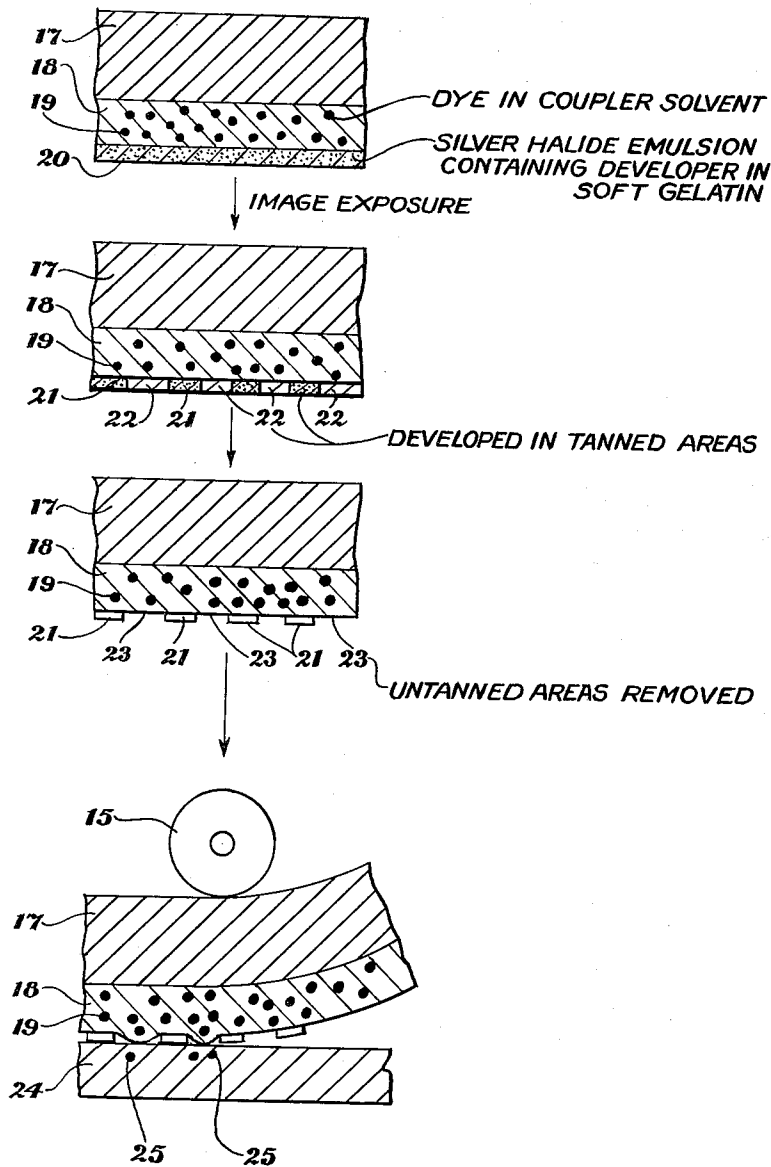
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2 Sheets-Sheet 2

Fig. 2



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3,012,885

PRESSURE IMAGE TRANSFER PROCESS

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This invention relates to photography and particularly to a process of transferring a photographic image by pressure.

Photographic images have been transferred from a printing original to a blank receiver in various ways, such as imbibition of dye, diffusion of salts or other image components, and transfer of image colloid. While pressure of the original against the receiver is involved to some extent in all of these methods, pressure has not been employed to squeeze or press the image out of the original into the receiver.

It is therefore an object of the present invention to provide a novel pressure image transfer method. A further object is to provide a method for transferring a colored image from a photographic emulsion layer to a receiving sheet. Other objects will appear from the following description of our invention.

These objects are accomplished according to our invention by first forming a dye image in a hydrophilic colloid layer of a photographic element having a silver halide emulsion layer, the colloid layer containing a dispersion of a solution of color-forming compound or coupler in an organic crystalloidal solvent for the coupler and the dye formed from it, having a boiling point above about 175° C., and then pressing the colloid layer containing the image into contact with an oil-absorbent receiving sheet with sufficient pressure to cause the organic solvent and dye image to transfer to the receiving sheet.

In the accompanying drawing,

FIG. 1 illustrates the steps in our process by means of sectional views of the film being treated, and

FIG. 2 illustrates a modification of our process also by means of sectional views of the film at successive stages in the process.

The material employed in the method of our invention is a hydrophilic colloid layer such as gelatin, coated on any suitable flexible support such as cellulose ester, paper or synthetic resin, containing in the gelatin or other hydrophilic colloid a dispersion of a solution of a coupler or dye in a solvent for the coupler or dye, and for the dye formed from the coupler.

The coupler is one which is capable of coupling with the oxidation product of a primary aromatic amino developing agent on photographic development, suitable couplers being disclosed in Jelley and Vittum U.S. Patent 2,322,027, Loria et al. U.S. Patent 2,600,788, McCrossen et al. U.S. patent application Serial No. 476,159, Thirtle and Weissberger U.S. patent application Serial No. 550,755 and Glass et al. U.S. Patent 2,521,908. Since the couplers of the latter patent are colored, they may also be considered dyes.

The solvent in which the coupler or dye is dissolved is an organic crystalloidal solvent for the coupler or dye, and for the dye formed from the coupler, having a boiling point above about 175° C. Suitable solvents include di-n-butyl phthalate, diethyl lauramide, tricresyl phosphate, and other coupler solvents disclosed in Jelley and Vittum U.S. Patent 2,322,027.

The coupler or dye is first dissolved in the organic solvent in any suitable ratio, such as 1 part of coupler or dye in from 1 to 10 parts of organic solvent. More or less coupler may, however, be employed. The solution is then dispersed in gelatin or other hydrophilic

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colloid, and this may be coated on the support as such, or mixed with a silver halide emulsion and coated. Two or more coatings of different couplers may be superposed on the support, or two or more dispersions of different couplers may be mixed in a single layer.

In the layer just described, the ratio of gelatin (or other hydrophilic colloid) to organic solvent is critical. This ratio should be one part of gelatin to from 1 to 5 parts of organic solvent, by weight. Since our process depends upon squeezing or pressing the solution of coupler or dye from the gelatin layer onto a receiving sheet, the amount of solution should be high in relation to the amount of gelatin in the layer. In the usual photographic layer containing a coupler dispersion, there is much less coupler and solvent solution in relation to the gelatin, than in the material which we use.

The manner in which our process produces an image will now be described, referring to the accompanying drawing as required.

As shown in FIG. 1, a support 10 is coated with a gelatino-silver halide layer 11 containing a dispersion of particles 12 of colorless coupler dissolved in the organic solvent. This layer is given an image exposure and is developed in a primary aromatic amino developing solution to produce a developed dye image where the layer was exposed, as shown by the solid dots 13 in the second stage of FIG. 1. The layer need not be fixed, but is preferably wiped dry with a squeegee, and is then placed face down on an absorbent receiving sheet 14 on a flat surface. A heavy roller 15 is then used to roll the two sheets tightly together. This presses the solvent and dye image 13 onto the receiving sheet 14, as shown at 16, leaving dye particles in the sheet 14 as a reproduction of the original colored image 13. Since not all of the original image is removed by the transfer, successive transfers may be made from the original to successive receiving sheets.

Another modification of our invention is shown in FIG. 2 of the drawing. In this modification, a support 17 of cellulose ester, paper or synthetic resin is coated with a gelatin layer 18 containing a dispersion 19 of a solution of dye in organic solvent. The layer 18 is therefore uniformly colored by the dye dispersion. This layer is overcoated with a layer 20 of silver halide in soft gelatin containing a tanning developing agent. This sensitive layer is of the type described in Yutzy and Yackel U.S. Patent 2,596,756.

Upon exposure of this element to a line or half-tone image and development as described more fully herein-after, developed and tanned gelatin areas 21 are produced where the layer 20 was exposed. Soft gelatin areas 22 remain in the unexposed areas. The gelatin in these areas is removed by washing the element with warm water, as shown at 23 in the third stage of FIG. 2.

By pressing this element against an absorbent receiving sheet 24 by means of roller 15, as shown in the last stage of FIG. 2, gelatin layer 18 is forced through the open spaces in layer 18, causing this layer to contact the receiving sheet 24 at those areas. The dispersed particles 19 are thereby caused to transfer to the receiving sheet as shown at 25, resulting in an image in the receiving sheet corresponding to the unexposed portions of the sensitive layer 20.

Our invention will be further explained by reference to the following specific examples:

Example 1

This example illustrates a single-layer coating.

A coating was made on cellulose acetate film base at a wet thickness of .005 inch, of an emulsion prepared as follows:

10 cc. of a gelatino-silver chloride emulsion containing

1 mole of silver chloride and 50 g. of gelatin (dry weight basis) per liter of emulsion was mixed with 5 cc. of a coupler dispersion prepared as follows:

Coupler ¹	grams--	5
Di-n-butyl phthalate.....	cc--	50
Gelatin, 10% solution.....	cc--	100
Alkanol B, 5% solution (alkyl naphthalene solution)	cc--	25

¹ 2-(2,4-di-n-amyphenoxyacetamino)-4,6-dichloro-5-methylphenol (Thirtle and Weissberger U.S. application Serial No. 550,755).

This mixture was passed through a colloid mill before mixing it with silver halide emulsion. The coating was dried and processed as follows:

The emulsion was exposed to a negative subject by Photo-flood light and processed for 30 seconds in a developer of the following composition:

	Grams
4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.....	2
Sodium sulfite (desiccated).....	4
Sodium carbonate, monohydrate.....	20
Sodium sulfate.....	100
Water to 1 liter.	

After development, the processed strip was wiped dry with a squeegee and placed face down on a piece of writing paper. The two sheets were pressed firmly together by rolling a heavy metal cylinder over them. The sheets were then stripped apart revealing a high density, transferred colored image having the invisible oily solvent containing the unreacted coupler in the non-image areas and oily solvent containing cyan dye in the image areas. Six successive transfers were made from the developed strip.

Example 2

This example describes a two-layer coating.

A red-sensitive emulsion layer was made by mixing 10 cc. of a coupler dispersion prepared as in Example 1, with 5 cc. of a red-sensitive gelatino-silver chlorobromide emulsion containing 0.278 mole of silver halide per liter of emulsion and coating the mixture on a cellulose acetate film support.

Over this emulsion there was coated a green-sensitive emulsion made by mixing 10 cc. of a coupler dispersion made as in Example 1 but replacing the coupler with 1 - (2',4',6' - trichlorophenyl) - 3 - [3'' - (2'',4''' - di-tert. - amyphenoxyacetamido)benzamido] - 5 - pyrazolone (U.S. Patent 2,600,788), with 5 cc. of a green-sensitive gelatino-silver chlorobromide emulsion containing 0.314 mole of silver halide per liter of emulsion.

The double coating was dried and exposed separately to a line subject through Wratten No. 61 filter (green) and Wratten No. 29 filter (red). Film was then developed for two minutes in the developer of Example 1 and treated for 10 seconds in a stop bath of a saturated solution of sodium sulfate with the pH adjusted to 3.0 with acetic acid. The surface of the coating was then wiped dry with a squeegee and rolled in contact with double weight photographic paper stock in a clothes wringer.

When the strips were separated there resulted a transferred line image of magenta and cyan dyes. The receiving sheet was then washed with water to remove any unreacted developer.

Example 3

The example illustrates a mixed coupler coating.

Five grams of a silver chloride emulsion containing 1 mole of silver chloride per liter of emulsion was mixed

with 8 grams of 10% gelatin solution and 20 grams of the following coupler dispersion:

Cyan coupler ¹	grams--	5
Magenta coupler ²	do--	10
Yellow coupler ³	do--	15
Di-n-butyl phthalate.....	cc--	50
Gelatin, 10% solution.....	cc--	100
Alkanol B, 5% solution.....	cc--	10

¹ 2-(α -di-tert-amyphenoxy-n-butyrylamino)-4,6-dichloro-5-methylphenol (Fierke and Chechak U.S. application Serial No. 476,561).

² Same as magenta coupler of Example 2.

³ 3-benzoylacetylamino-4-methoxy-(2',4'-di-tert-amyphenoxy)acetanilide (McCrosen et al. U.S. patent application Serial No. 476,159).

The coupler dispersion passed through a colloid mill before mixing with the emulsion, and the mixture was coated at a wet thickness of .002 inch and dried.

The coating was exposed through a continuous tone step wedge, line negative, and half-tone positive, respectively. The three exposed strips were processed for 30 seconds in the developer of Example 1 and the coating was wiped dry with a squeegee and rolled in contact with a double weight photographic paper stock in a clothes wringer.

When the strips were separated, there resulted a neutral tone transferred line image with very high sharpness and clean background, smooth continuous tone image from the continuous tone step wedge but one which was not equal in tone because of unequal coupling rates of the couplers from the line negative, and a half-tone image with very sharp dots from the half-tone positive.

Example 4

This example describes transferring a dye dispersion through a gelatin matrix.

A cellulose ester film base was coated with a dye dispersion made as follows:

100 cc. of a 10% aqueous gelatin solution was mixed with a solution of 10 grams of 1-hydroxy-4-phenylazo-4'-(p-tert-butylphenoxy)-2-naphthanilide in 60 cc. of diethyl lauramide, and 15 cc. of 5% aqueous Alkanol B solution with enough water to make 200 grams of solution. This mixture was milled five times in a colloid mill and one part by weight of the dispersion was added to one part by weight of a 10% aqueous gelatin solution. After stirring thoroughly, the mixture was coated on the support giving, when dried, a coating containing .720 gram of gelatin, .240 gram of dye and 1.44 grams of diethyl lauramide per square foot.

A second layer of silver chloride emulsion containing tanning developing agent was coated on the gelatin layer containing the dye dispersion. This emulsion was prepared from a gelatino-silver chloride emulsion containing one mole of silver chloride in 3600 grams of emulsion, and was mixed with the following ingredients:

Emulsion	grams--	72
Methylene Blue solution (1 mg. per 10 cc. of water)	cc--	4
Dispersion of 4-phenyl catechol.....	grams--	18
Gelatin (10% solution).....	do--	20.6
Saponin (15% solution).....	cc--	2
Water	cc--	39.4
Total	grams--	156

The dispersion of 4-phenyl catechol which is the tanning developing agent was made by adding a solution of 50 grams of 4-phenyl catechol in 50 cc. of tricresyl phosphate to a mixture of 500 cc. of 10% gelatin solution and 15 cc. of 15% saponin solution and adding water to give 700 grams total mixture. This mixture was milled five times in a colloid mill before adding it to the emulsion.

The second layer was coated over the first and dried.

The emulsion was exposed to a high contrast positive transparency and processed for 20 seconds in an aqueous

solution of sodium carbonate and urea containing 4% sodium carbonate and 5% urea. Samples were immersed in the solution at 80° F., 88° F. and 98° F. The element was then placed with the emulsion in contact with an unsized paper stock and passed through a clothes wringer. After three passes through the wringer, the untanned gelatin was removed from the unexposed portions of the emulsion and 10 subsequent transfers could then be made to separate sheets of paper to produce a dye image by squeezing dye through the areas where the unhardened gelatin had been removed. The same result occurred with the matrix developed at the different temperatures stated above, but at the higher temperatures, the unexposed gelatin was more quickly removed.

Numerous variations may, of course, be made in our process without departing from the scope of our invention. For example, the ratio of coupler to coupler solvent, the ratio of gelatin to coupler solvent, the temperature at the time of transfer, and the transfer pressure, may all be varied over a wide range. These variations are illustrated by the tests now to be described.

A series of coatings was made as in Example 1, using plain gelatin instead of silver halide emulsion, and employing the coupler 2-(α -di-tert.-amylphenoxy-n-butylamino)-4,6-dichloro-5-methyl phenol (Fierke and Chachak U.S. patent application Serial No. 476,561, now U.S. Patent No. 2,801,171). The coatings were so designed that each contained 0.540 gram of gelatin (calculated as dry gelatin) and 0.345 gram of coupler per square foot of film base on which the dispersions were coated. The amount of coupler solvent was varied as shown in the following table:

Coating No.	I	II	III	IV	V
Gelating weight	.540	.540	.540	.540	.540
Coupler weight	.345	.345	.345	.345	.345
Ratio coupler to coupler solvent	1:1	1:2	1:4	1:6	1:8
Ratio gelatin to coupler solvent	1:1.65	1:1.3	1:2.5	1:3.8	1:5

A squeezing device was made so that the transfer pressure could be varied from 1 kg. per sq. cm. to 11 kg. per sq. cm. Transfers were then made from the various samples to the baryta side of baryta-coated paper, employing various pressures and temperatures. This transferred uncolored coupler and coupler solvent to the paper. The paper samples were dipped into a solution of 2 grams of 2-amino-5-diethylamino toluene and 5 g. of sodium sulfite per liter of water, and then into an oxidizing solution of 10 g. of potassium ferricyanide and 20 g. of sodium carbonate per liter of water to oxidize the developer and form a uniform dye image where sufficient coupler had transferred.

The results with respect to pressure variation at a transfer temperature of 72° F. and transfer time of 1 minute are shown in the following table. The amount of transfer is indicated as follows:

0=trace
+=medium
++=high
+++ =highest

Coating No.	1 kg. per sq. cm.	2 kg. per sq. cm.	3 kg. per sq. cm.	6 kg. per sq. cm.	11 kg. per sq. cm.
I	None	None	None	None	None
II	None	0	0	0	+
III	0	0	0	+	++
IV	0	0	0	+	++
V	+++	+++	+++	+++	+++

The results with respect to temperature variation at a transfer pressure of 6 kg. per sq. cm. and transfer time

of 1 minute are shown in the following table, the amount of transfer being indicated as before.

Coating No.	80° F.	90° F.	100° F.	110° F.	125° F.
I	0	0	0	0	+
II	+	+	+	+	++
III	++	++	++	++	+++
IV	+++	+++	+++	+++	+++

No results are shown for variation in time of transfer, because variation of time from a fraction of a minute to several minutes made no difference in the results.

Instead of the coupler solvents described above, it is possible to use a high-melting-point hydrocarbon wax. In this case it is necessary to apply heat as well as pressure to obtain an image transfer.

It will be understood that the examples and modifications described above are illustrative only, and that our invention is to be taken as limited only by the scope of the appended claims.

What we claim is:

1. The method of forming a dye image in an oil-absorbent receiving sheet by transfer, which comprises forming a coupler compound image by exposure and color development with a primary aromatic amino developing agent, in a light-sensitive element including a layer of hydrophilic colloid containing a dispersion of a coupler compound capable of reacting with the oxidation product of a primary aromatic amino developing agent to form a dye, said coupler compound being dissolved in an organic crystalloidal solvent for the coupler and for the dye formed therefrom and having a boiling point above about 175° C., the ratio of hydrophilic colloid to organic solvent being between about 1 to 1 and 1 to 5, and while retaining said hydrophilic colloid in said layer, pressing said element into contact with an oil-absorbent receiving sheet with sufficient pressure to cause said organic solvent and coupler compound image to transfer to said receiving sheet.

2. The method of transferring a dye image from a photographic emulsion layer to an oil-absorbent receiving sheet, which comprises forming a dye image by exposure and color development with a primary aromatic amino developing agent, in a gelatino-silver halide emulsion layer containing a dispersion of a color coupler capable of reacting with the oxidation product of a primary aromatic amino developing agent in an organic crystalloidal solvent having a boiling point above about 175° C., the ratio of gelatin to organic solvent being between about 1 to 1 and 1 to 5, and while retaining said gelatin in said layer, pressing said layer into contact with an oil-absorbent receiving sheet with sufficient pressure to cause said organic solvent and dye image to transfer to said receiving sheet.

3. The method of transferring a dye image from a photographic emulsion layer to an oil-absorbent receiving sheet, which comprises forming a dye image by exposure and color development with a primary aromatic amino developing agent, in a gelatino-silver halide emulsion layer containing a dispersion of di-n-butyl phthalate having dissolved therein a color coupler capable of reacting with the oxidation product of a primary aromatic amino developing agent, the ratio of gelatin to di-n-butyl phthalate being between 1 to 1 and 1 to 5, and while retaining said gelatin in said layer, pressing said layer into contact with an oil-absorbent receiving sheet with a pressure of 1 to 11 kilograms per square meter to cause said di-n-butyl phthalate and dye image to transfer to said receiving sheet.

4. The method of transferring a dye image from a photographic emulsion layer to an oil-absorbent receiving sheet, which comprises forming a dye image by exposure and color development with a primary aromatic amino

developing agent, in a gelatino-silver halide emulsion layer containing a dispersion of di-n-butyl phthalate having dissolved therein 2-(2,4-di-n-amyphenoxyacetamino)-4,6-dichloro-5-methylphenol, the ratio of gelatin to di-n-butyl phthalate being approximately 1 to 5, and while retaining said gelatin in said layer, pressing said layer into contact with an oil-absorbent receiving sheet with a pressure of 1 to 11 kilograms per square meter to cause said di-n-butyl phthalate and dye image to transfer to said receiving sheet.

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References Cited in the file of this patent

UNITED STATES PATENTS

853,863	Connolly	May 14, 1907
1,935,477	Martinez	Nov. 14, 1933
1,981,794	Williams	Nov. 20, 1934
2,322,027	Jelley et al.	June 15, 1943
2,543,181	Land	Feb. 27, 1951
2,756,143	Murray	July 24, 1956
2,787,544	Godowsky et al.	Apr. 2, 1957
2,852,382	Illingsworth et al.	Sept. 16, 1958