Dec. 5, 1961 D. A. NEWMAN 3,011,905

MANIFOLD SYSTEM COMPRISING REACTANT DONOR AND RECEPTOR SHEETS

Filed Sept. 9, 1959

Fig. 1

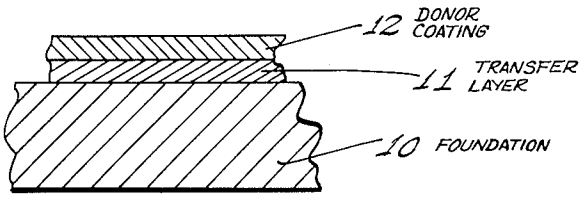


Fig. 2

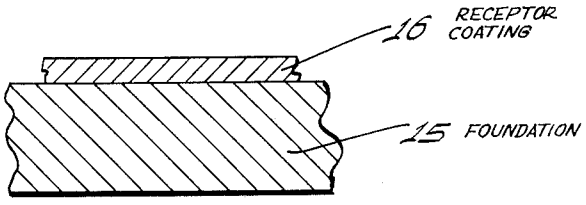
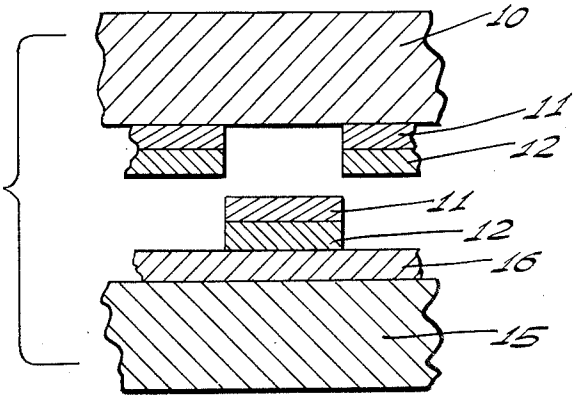


Fig. 3



INVENTOR.

Douglas A. Newman

BY

Johnson and Kline

ATTORNEYS

United States Patent Office 3,011,905
Patented Dec. 5, 1961

3,011,905

MANIFOLD SYSTEM COMPRISING REACTANT DONOR AND RECEPTOR SHEETS

Douglas A. Newman, Glen Cove, N.Y., assignor to Columbia Ribbon and Carbon Manufacturing Company, Inc., Glen Cove, N.Y., a corporation of New York

Filed Sept. 9, 1959, Ser. No. 838,922
13 Claims. (Cl. 117—33.3)

This invention relates to a manifolding paper, and relates more particularly to what is now commonly known as "carbonless copy." By means of such manifolding paper a number of copies may be made simultaneously by applying pressure or impact on a top sheet without the necessity of inserting carbon paper between each sheet of copy.

The carbon paper as normally employed is provided on one surface with an ink layer, which ink surface is placed adjacent the surface of a sheet of copy paper which is to receive the impression or image. Pressure on the original sheet on top of the carbon paper causes transfer of ink to the copy surface of the paper sheet. One of the main disadvantages of conventional carbon paper is that the use thereof often results in a soiled copy sheet, soiled hands and a copy which is extremely susceptible to smudging.

To overcome these defects of carbon paper use, it has been proposed to use a carbonless copy, i.e. a copy prepared by the employment of a paper sheet having applied to the back of the same a colorless chemical which by reaction with a colorless chemical on the face of the adjacent copy sheet produces an image or mark on said face of said copy sheet when pressure is applied on the top sheet as by the type face of a typewriter key or by the point of a writing instrument through chemical reaction. The two chemical coatings may be classified as "complemental color formers."

While these so-called "carbonless copy papers" heretofore used avoided the smudging risk ever present when ordinary carbon papers are employed, they were nevertheless possessed of certain disadvantages which seriously diminished their utility. The greatest disadvantage resided in the fact that the image formed gradually lightened in color, and in some cases disappeared due to the effects of air, humidity, moisture or destructive light waves. For instance, where the formed image is composed of cupric thiocyanate and the copy paper is stored, humidity and moisture attack the cupric thiocyanate changing it by reduction from the black cupric to the colorless cuprous thiocyanate. Another disadvantage resided in the fact that there was a simultaneous transfer of the two complemental ingredients in both directions with the result that back printing, i.e. printing on the reverse side, took place on the original or top sheet as well as copy production on the front of the copy sheet. Furthermore, the color-forming reactions were generally ionic in nature and thereby required the presence of at least a minimum amount of moisture in either the top sheet or the copy sheet or in both sheets. Accordingly, even when the papers were initially treated with moisture, they still had only a short shelf-life and became useless when they dried out. Still other disadvantages of prior carbonless copies were that the color of the imprint was a blue which was often not readily readable, that the imprint took an appreciable time to develop, and that the imprint was not reproducible by machine using thermographic or other heat-employing processes.

It is therefore an important object of this invention to provide a carbonless copy which will be free from the foregoing and other disadvantages and which will produce a clean, sharp, smudge-free copy which is particularly

stable and long-lasting due to its protection against moisture, air and destructive light waves.

Another important object of the present invention is to prepare carbonless manifolding sheets in which the donor chemical is transferred completely from the impressed areas of the donor sheet to the surface of the adjacent receptor sheet where all of the chemical is available for reaction with the receptor chemical. This prevents waste of the donor chemical and also provides darker and more permanent images than possible up to this time.

Another object of this invention is the provision of a carbonless copy in which the transfer of the complemental ingredients will take place only from the back of the original sheet to the front of the copy sheet, thus completely eliminating back printing on the original sheet.

A further object of this invention is the provision of a carbonless copy medium in which at least one of the coatings, while dry to the touch, contains non-drying ingredients including sufficient moisture to provide the aqueous medium necessary for the color-forming reaction when required, and thus result in a product that may be stored for a long period of time without being subject to drying out or other deterioration.

Still another object of this invention is to provide a carbonless copy which is long-lasting and durable and which, when used in pack form, is stabilized against detrimental migration through the sheet of the complementary color-forming chemicals which are, in the principal form of the invention, coated on opposite sides of the same sheet.

Another object of this invention is the provision of of a carbonless copy which is reproducible by the Thermofax and other heat-employing processes.

Other objects and advantages of this invention will appear from the following detailed description.

In the drawing:

FIGURE 1 is a fragmentary diagrammatic section, to an enlarged scale, of the donor sheet described herein.

FIG. 2 is a fragmentary diagrammatic section, to an enlarged scale, of the receptor sheet described herein.

FIG. 3 is a fragmentary diagrammatic section, to an enlarged scale, of the receptor sheet after transfer of the donor chemical and wax thereto.

In general, the carbonless copy method of the present invention comprises a "donor" coating carried on the surface of a pressure-transferable wax coating which is in turn carried on the back of the original or top sheet and a "receptor" coating carried on the front or image side of the copy sheet. It should be understood that the copy sheet itself can carry on the back thereof a pressure-transferable coating overcoated with a donor coating, thus permitting the production of many copies simultaneously. The donor sheet, exemplified by FIG. 1 of the drawing, comprises a fundation sheet **10** coated with a pressure-transferable layer **11** and a supercoating of a color-forming ingredient carried in a binder **12**. The acceptor sheet, exemplified by FIG. 2 of the drawing, comprises a foundation sheet **15** which is coated with a layer of a chemical **16** which is complementary to the chemical on the donor sheet and which reacts therewith on contact in the presence of moisture to form a visible image.

The pressure-transferable undercoating layer on the donor sheet serves many purposes. Primarily, it serves as a stabilizer or permanentizer for the formed image, thus overcoming a serious problem found in the use of the prior art carbonless sheets. Since the layer is transferred under pressure along with the color-forming chemical and its binder, then the result is the formation of an image which is insulated from air and moisture by a pressure-transferable overcoating, as exemplified by FIG.

3. In other cases where the lightening or disappearance of the formed image is caused by the harmful rays of the sun rather than the effects of air and moisture, then it is particularly effective to include an ultraviolet light absorbing compound in the wax protective layer on the donor sheet. Conventional ultraviolet absorbers may be employed, such compounds being in general carbonyl-containing compounds, among which are benzoyl resorcinol, benzophenone, substituted benzophenones, such as dihydroxy benzophenone and 2,2'-dihydroxy-4n-octoxy benzophenone sold by American Cyanamid under the name Cyasorb UV 314. Also used with great success are the salicylate and benzoate esters such as phenyl salicylate (Salol) and dibenzoyl resorcinol. Amounts in the range of 0.01–8 percent based upon the weight of the undercoating have been found effective while a preferred range lies between 0.1 to 5.0 percent. Also it has been found that a more lasting image results where a combination of color-forming chemicals is employed. For instance, gallic acid is added to the transfer layer **10** and a copper salt such as copper sulfate is employed as the color-forming chemical in layer **11**. Receptor layer **16** contains a combination of complementary color-forming chemicals such as ferric chloride and sodium thiocyanate. Under pressure of a pencil, pen or stylus, an image results immediately due to the speedy reaction of the thiocyanate and the copper salt to form black (cupric thiocyanate) $Cu(SCN)_2$. However, the deep black tone is maintained due to the slower migration and reaction speed of the gallic acid from the wax layer into layers **12** and finally **16** where a black color results slowly upon contact with the ferric salt. This delayed reaction in combination with the protective overcoat results in a particularly stable image. Of course, here also, if the need dictates, a conventional ultraviolet absorber may be included in the wax protective layer.

For example, in the preferred form and in particular the foundation which is to form the donor sheet is coated with a pressure-transferable composition of the type conventionally employed in duplication. Such composition may be comprised of any frangible material such as the plasticized or softened cellulose bases, for instance, ethyl cellulose containing oil modified glycol sebacate, natural resins such as rosin, or any frangible wax. In the preferred embodiment of the present invention, a pressure-transferable wax layer is employed. Conventional waxes which are used are those of the animal, vegetable, mineral or synthetic, original such as carnauba, raw montan wax, beeswax, ceresin, paraffin, microcrystalline wax, carbowax, spermaceti, solid esters or other hot melt frangible film formers, alone or in combination with each other or with lanolin and/or mineral oil. Conventional filler compounds may also be included where desired.

Next a coating of the color-forming chemical carried in a binder is applied to the wax surface. The binder may be resinous or film-forming. Materials which are particularly well adapted herein as binders in either the donor or receptor sheet are gelatin, casein, starch, polyethylene glycols, vinyl alcohol, carboxymethyl cellulose, hydroxyethyl cellulose and various other cellulose ethers such as methyl and ethyl cellulose and water-dispersible or miscible colloidal binders. The nature of the color-former is not particularly critical so long as the chemicals employed in the donor and receptor coatings are responsive to each other so that they react to form an image which is clearly legible on the copy sheet. In most instances the formation of a black image is preferred, but of course there are instances where red copy is convenient, such as in the preparation of debit sheets. Virtually any color may be obtained by the substitution of one color-forming compound for another, and the brightly colored copy images are very clearly legible particularly where a dark colored copy sheet is used as the background.

In use, the donor coating on the back face of the original sheet is placed face down on the receptor coating

which is on the front face of the copy sheet. If more than one copy is desired a plurality of copy sheets, provided with donor coatings on their reverse sides, or back faces, are place one on top of the other as in the conventional procedure for making plural carbon copies. The pressure produced by the point of the writing instrument or typing on the top sheet is sufficient to transfer both the color-forming chemical, such as sodium thiocyanate, and the pressure-transferable wax donor coating to the receptor coating. Since the gelatin in the latter coating, even when dry to the touch, contains a certain amount of bound water and since most thiocyanates are to varying degrees hygroscopic, thus in effect supplying their own moisture, sufficient moisture is provided for the instantaneous formation of the colored cupric thiocyanate image. The pressure produced by the writing instrument or the impact of the type face transfers some of the thiocyanate and wax from the donor coating onto the receptor coating in contact therewith. Since the latter is substantially dry there is no migration of the copper salt to the donor coating, thus completely eliminating back printing on the original sheet.

The following examples will illustrate preferred modes for practicing the invention. It will be recognized by those skilled in the art that the examples are merely illustrative, but not limitative.

COLOR-FORMING DONOR COATINGS

Donor coating A

A typical color-forming donor coating is formulated as follows:

	Gms.
Sodium thiocyanate	20
Lanolin	15
Toluene	20
Butyl stearate	10
Ethyl cellulose	15
Alcohol	85
(Filler) kaolin, barium sulphate, etc.	25

The butyl stearate is slowly added to the sodium thiocyanate while grinding. The lanolin and a portion of the toluene are warmed together until the lanolin dissolves, and the solution is added to the sodium thiocyanate-butyl stearate mixture. The ethyl cellulose is then dissolved in the alcohol and the balance of the toluene. This solution is stirred into the mixture containing sodium thiocyanate, butyl stearate, lanolin and the first portion of toluene.

When thoroughly mixed, the composition is applied as a coating to sheets of the wax coated paper, and the latter then warmed to remove volatile solvents. Some moisture remains within the dried film.

If the optional kaolin filler is used, the sodium thiocyanate is first ground with the kaolin and the butyl stearate then added slowly to the ground thiocyanate-kaolin mixture. Where a filler is used, more butyl stearate than that specified above will be needed, the exact amount depending on the amount of filler and the desired viscosity of the finished composition.

In the above formulation, a water-soluble binder such as methyl cellulose, hydroxyethyl cellulose or carboxymethyl cellulose may be substituted for the ethyl cellulose with the corresponding change in solvent from alcohol to water.

Donor coating B

A typical color-forming donor coating employing gallic acid is formulated as follows:

Polyethylene glycol(s)	gms.	7
Gallic acid	gms.	8
Clay	gms.	8
Alcohol	cc.	40

The gallic acid in the above formula is ground and dispersed in the solution containing the glycol(s) and

alcohol and the coating may then be applied over the pressure-transferable wax coating of the donor sheet in a conventional manner, as for example by print coating (Anilox method).

COLOR-FORMING RECEPTOR COATINGS

Receptor coating A

A typical receptor coating to be used with donor coating A is formulated as follows:

	Gms.
Kaolin	30
Copper sulfate	30
Water	100
1% gelatin solution	50

The kaolin and copper sulfate are ground together and 100 grams of water are slowly added while grinding. The mixture is thoroughly stirred and then dried. When dried the solids are ground to a smooth powder. A gelatin solution is then made by heating 0.5 gram of gelatin in 50 grams of water until the gelatin is dissolved. This gelatin solution is added slowly to the powder with continuous grinding. The resulting mixture is then coated on a sheet of paper which is dried until no moisture can be felt by touching it. However, there remains a significant amount of internal moisture within the gelatin film.

Receptor coating B

A typical receptor coating to be used in conjunction with donor coating B is formulated as follows:

	Gms.
Cellosize 3 #78WP300 (hydroxyethyl cellulose)	½
Water	25
Clay	6
Polyethylene glycol	3
Nulomoline (invert sugar)	2
Glycerine	8
$FeCl_3$	3
Methanol	2

In use, the sheet of paper having the color-forming donor coating is placed coating down on a sheet carrying the receptor coating so that the two coatings are face-to-face. The top sheet may then be used for writing or typing purposes to produce an original and a copy.

The color of the copy will, of course, depend upon the particular combination of reactants which are used. Thus, in the examples described above, a thiocyanate with a copper salt produces a black copy. An iron salt used in place of copper will produce a red copy, while cobalt salts will produce a blue copy.

Likewise in the gallic acid-iron system, when ferric chloride is used in the receptor layer, a black color results upon contact with the gallic acid. Substitution of the ferric chloride with sodium ferrocyanide results in a blue color upon contact with the gallic acid. Any variety of substitutions may be made according to the colors desired. For instance, when a red color is desired, nickel salts and glyoxime may be used in place of the iron salts and gallic acid in the above B system.

The invention is not limited to the precise proportions and components set forth in the foregoing example.

Thus, increasing the amount of sodium thiocyanate will intensify the color of the copy, while varying the amount and type of filler will modify the writing qualities of the paper. If more of the non-drying liquid phase which constitutes the plasticizing component of the donor coating is used, the resultant product will be more sensitive and responsive to pressure. It will be obvious that optimum proportions can be varied and selected within the scope of the invention, depending on the desired end use.

In place of sodium thiocyanate of donor coating A, there can also be used other compounds such as potassium thiocyanate, ammonium thiocyanate, tetramethyl ammonium thiocyanate, tritolyl thiocyanate, trimethyl thiocyanate and tolyl thiocyanate.

The copper sulfate of receptor coating A may also be replaced by other compounds which will form highly colored reaction products with the above salts. The following salts have been found suitable for color formation when the thiocyanate is employed in the complementary sheet: cupric chloride, copper arsenite (in acid medium), copper ammonium chloride, copper carbonate (in acid medium), copper acetate, cupric potassium sulfate, cupric ammonium sulfate, cupric sulfide, cuprous oxide (in acid medium), chromium trioxide, chromium acetate, chromic acid, and the aforesaid salts of manganese, lead and iron, etc.

In place of the gallic acid of donor coating B there can also be used alkyl gallates, pyrogallol, gallo-tannic acid, tannin, logwood extract containing hematoxylin, dihydroxynaphthalene, salicylic acid, oxymestiylenic acid and other hydroxyaromatic compounds.

Some iron salts which have been found useful in receptor coating B are ferric chloride, ferric ammonium sulphate, iron glycerol phosphoric acid, sodium ferrocyanide, iron oxide, ferric sulphate, ferric benzoate, and many others.

No particular criticality exists in the selection of the color-forming chemicals. It is usually preferred that both the donor and receptor chemicals be colorless and that the colored reaction product be black, as is the case with the aforementioned chemicals. However, where a blue copy is desired, a ferrocyanide or ferricyanide such as the sodium or potassium salt may form the donor chemical and an iron salt such as those mentioned above may form the receptor chemical in which case the image formed is of Prussion blue or Turnbull's blue. Likewise cobalt salts form a blue reaction product with thiocyanates.

If a red color is desired, a thiocyanate donor chemical and an iron receptor chemical may be used. Or else glyoxime may form the donor coating and a nickel salt such as the sulphate may form the receptor coating to produce a bright red copy.

Where an orange or yellow image is desirable, a ferricyanide or a ferrocyanide forms the donor chemical and a silver salt such as the nitrate forms the receptor coating. Upon reaction the respective orange and yellow colors result.

Moreover, the kaolin filler may be substituted in whole or in part by infusorial earth, starch, celite or cab-o-sil.

The amount of solvent to be used in the foregoing formulations will be dictated by the particular methods employed for applying the coatings to the paper, that is, different methods require different viscosities and therefore different solvent contents. Thus, for example, when a reverse roll coater is used, it is desirable that the coating composition be rather viscous, whereas an equalizer blade coating operation requires a thinner or less viscous composition. The quantities set forth in the foregoing example of the donor coating have been satisfactory for equalizer blade coating.

Similar considerations apply to the coating of the acceptor sheet. In place of gelatin, there can also be used carboxymethyl cellulose, starch, or any other water-dispersible colloid. Furthermore, if the drying means of the coating machine causes too much moisture in the coat to be driven off, any suitable well-known humectant may be added to supply the necessary moisture for the color-forming reaction.

Where coatings are made employing sodium thiocyanate in the donor coating and copper sulphate in the receptor coating as in the formulations set out above, the reaction which occurs is as follows:

$$CuSO_4 + 2NaSCN \rightarrow Cu(SCN)_2 + Na_2SO_4$$

The cupric thiocyanate which is formed is black. More generally, the important part of the reaction is the for-

mation of the black $Cu(SCN)_2$; therefore, other copper salts and other cyanates yielding cupric thiocyanate, similar to the examples already mentioned, are applicable to this process. Other combinations of metal salts and thiocyanates also serve where they result in the formation of metal thiocyanates of suitable color. Likewise any combination of an iron salt and gallic acid is entirely suitable in that a black color results. Reactions whose constituents can be separated and placed into the separate coatings, and which will react upon contact when writing pressure is applied to yield a product or products of suitable color, are applicable to this system. For example, if the triazine component of a Rapidogen type dye such as Neutrazoic FFM (Black) (Atlantic Dye Corp.) is put into one coating and the dye coupling agent, such as a naphthalene sulfonic acid, is placed in the other coating, a copy results when writing pressure brings the coupler and dye into contact.

With the present reaction system it has been found that the reaction occurs best when the pH of the medium is in the neutral or slightly acid range. The copper salt should be held firmly in the receptor coat, but the surface of the particles must be exposed so that they can come in contact with the thiocyanate when it is released by the donor coat. The thiocyanate is finely dispersed in the butyl stearate, but is released when normal writing pressure is exerted, allowing the particles of thiocyanate and copper salt to come in contact.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

I claim:

1. A manifolding system comprising superimposed sheets having contacting faces, one of said sheets having thereon a donor coating coated over a layer of pressure-transferable material on the sheet, said donor coating including a first color-forming ingredient, the other of said contacting faces having a receptor coating thereon including a second color-forming ingredient, capable of reacting with said first color-forming ingredient to produce a legible colored reaction product, dispersed in a moisture containing film, said donor sheet being capable of relinquishing said first color-forming ingredient and said pressure-transferable material upon application of pressure to the uncoated surface of the donor sheet whereby, upon application of such pressure, an amount of said pressure-transferable material and said first color-forming ingredient is transferred to the receptor coating, thereby reacting with the second color-forming ingredient to produce an overcoated colored image which is particularly stable and long-lasting, due to its insulation from air and moisture and which corresponds in shape to the area over which pressure was applied.

2. The system of claim 1 in which the color-forming ingredient of the donor sheet is present dispersed in a hygroscophic binder material.

3. The system of claim 1 wherein the first color-forming ingredient is a thiocyanate and wherein the second color-forming ingredient is the salt of a metal capable of reacting with said thiocyanate to form a highly colored reaction product.

4. The system of claim 1 in which the first color-forming ingredient is a hydroxyaromatic compound and the second color-forming ingredient is the salt of a metal capable of reacting with said hydroxyaromatic compound to form a highly colored reaction product.

5. The system of claim 1 in which the first color-forming ingredient is a mixture of a thiocyanate and a hydroxyaromatic compound and wherein the second color-forming ingredient is the salt of a metal capable of reacting with both components of said first color-forming ingredient to form a highly colored reaction product.

6. The system of claim 1 wherein the layer of pressure-transferable material on the donor sheet contains a conventional ultraviolet light absorbing agent to prevent the lightening and disappearance of the formed images due to harmful rays.

7. A manifolding system comprising superimposed sheets of paper having contacting faces, the contacting face of the top sheet having thereon a donor coating coated over a layer of pressure-transferable wax on the sheet, said donor coating including a thiocyanate dispersed in a hygroscopic binder material, the contacting face of the other sheet having a receptor coating thereon including a salt of a metal, capable of reacting with said donor coating to form a highly colored reaction product, dispersed in a moisture-containing adhesive binder, said top sheet being capable of relinquishing an amount of the wax and donor coating to the receptor coating upon application of pressure to the uncoated side of the sheet having the donor coating, whereby the donor coating and metal salt react to form a colored image which is particularly stable and long-lasting due to its insulation from air and moisture and which corresponds in shape to the area of applied pressure.

8. The system of claim 7 wherein the thiocyanate is a member of the group consisting of sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, tetramethyl ammonium thiocyanate, tritolyl thiocyanate, tolyl thiocyanate, and trimethyl thiocyanate.

9. The system of claim 7 wherein the metal salt capable of reacting with the thiocyanate is a copper salt.

10. The system of claim 7 wherein the donor coating also contains a hydroxyaromatic compound.

11. The system of claim 7 wherein the wax on the donor sheet contains a conventional ultraviolet light absorbing agent to prevent the lightening and disappearance of the formed images due to harmful rays.

12. A manifolding system comprising superimposed sheets of paper having contacting faces, the contacting face of the top sheet having thereon a donor coating coated over a layer of pressure-transferable wax on the sheet, said donor coating including a mixture of a thiocyanate and a gallic acid dispersed in a hygroscopic binder material, the contacting face of the other sheet having a receptor coating thereon including a salt of a metal, capable of reacting with said donor coating to form a highly colored reaction product, dispersed in a moisture-containing adhesive binder, said top sheet being capable of relinquishing an amount of the wax and donor coating to the receptor coating upon application of pressure to the uncoated side of the sheet having the donor coating, whereby the donor coating and metal salt react to form a colored image which is particularly stable and long-lasting due to its insulation from air and moisture and which corresponds in shape to the area of applied pressure.

13. The system of claim 12 wherein the donor coating includes a mixture of sodium thiocyanate and gallic acid and the receptor coating includes an iron salt.

References Cited in the file of this patent

UNITED STATES PATENTS

2,168,098	Groak	Aug. 1, 1939
2,505,471	Green	Apr. 25, 1950
2,663,579	Zimmerman	Dec. 22, 1953
2,748,024	Klimkowski et al.	May 29, 1956
2,755,201	Webber	July 17, 1956
2,912,344	Newman et al.	Nov. 10, 1959