Jan. 15, 1963 E. J. METS 3,073,720

METHOD OF PROTECTING METAL FROM CORROSION

Filed March 23, 1960 2 Sheets-Sheet 1

Fig.3.

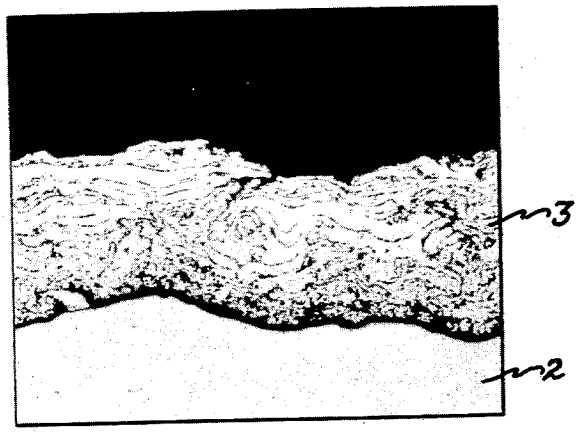
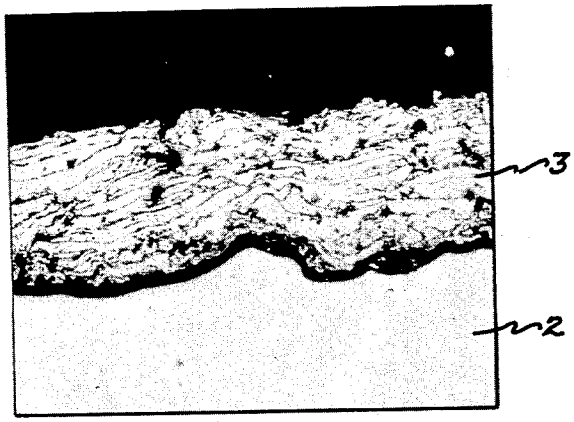



Fig.2.



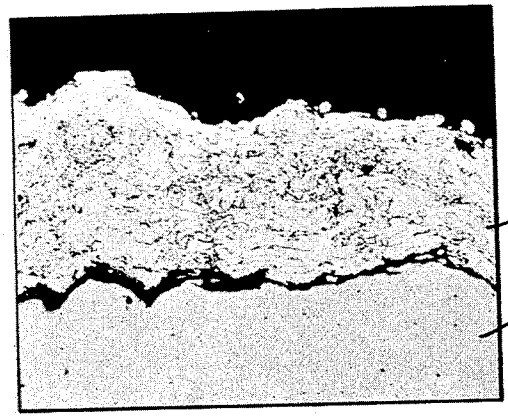




Fig.1.

Inventor,
Edwin J. Mets,
by Gilbert P. Tarleton
His Attorney.

Jan. 15, 1963 E. J. METS 3,073,720

METHOD OF PROTECTING METAL FROM CORROSION

Filed March 23, 1960 2 Sheets-Sheet 2

Fig. 4.

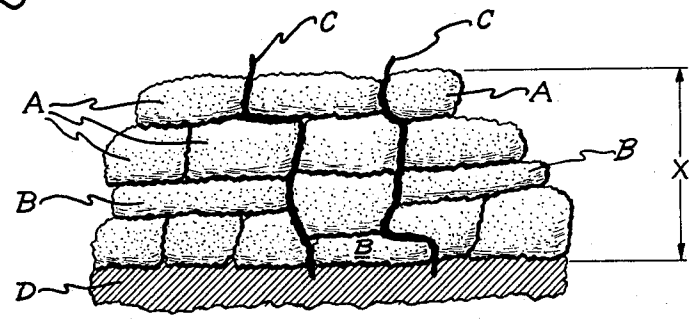
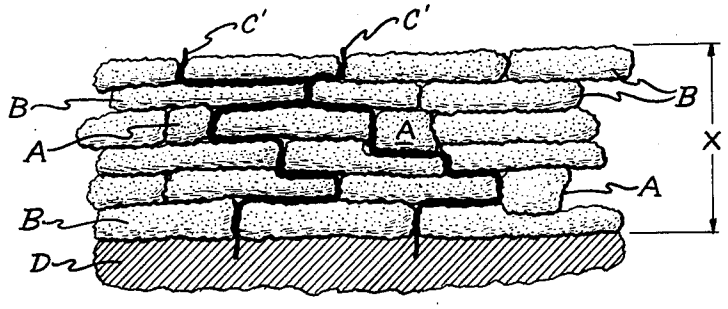



Fig. 5.




Inventor,
Edwin J. Mets,
by Gilbert P. Talbot
His Attorney.

United States Patent Office

3,073,720
Patented Jan. 15, 1963



# 3,073,720
# METHOD OF PROTECTING METAL FROM CORROSION

Edwin J. Mets, Auburn, N.Y., assignor to General Electric Company, a corporation of New York

Filed Mar. 23, 1960, Ser. No. 17,220
8 Claims. (Cl. 117—105)

The present invention relates to corrosion-resistant coatings for metals, and more particularly to spray-applied aluminum alloy coatings.

It is well known in the art that aluminum is a superior metal for coating other metals such as ferrous alloys because aluminum is resistant to corrosion, has a pleasing appearance, and also provides an excellent base for additional coatings, such as paint and varnishes. Consequently, considerable effort has been expended in developing aluminum alloy coatings and methods of depositing them on base metals. In commercial practice the two methods of depositing aluminum or ferrous metals most widely employed are the hot dipping of the ferrous metal in molten aluminum, and the spraying of molten aluminum on the ferrous metals by methods such as the Schoop process. The hot dip method provides a relatively nonporous coating that bonds well because a ferrous-aluminum alloy is formed between the surface coating of aluminum and the base of ferrous metal, due to the ferrous metal diffusing and alloying with the aluminum when the former is dipped into molten aluminum. Consequently, excellent corrosion resistance is provided by such a coating. The hot dip process, however, is not practical in all commercial operations because the article made from the ferrous metal is often of such a large size that it cannot be dipped into a molten bath of aluminum in any practical arrangement. An example of an article made of ferrous metal requiring a corrosion inhibiting coating that was too large to be hot dipped and had to be spray coated in accordance with my invention is an enclosure tank for an electrical transformer. Also, relatively thick alloy layer coatings are obtained by hot dipping, and thick coatings tend to fail on flexure because of inherent brittleness. Consequently, in coating articles of relatively large size, and for coating selective areas, the metal spraying process is essentially the only practical method by which aluminum can be deposited on ferrous metals. However, the nature of the coating structure obtained by metal spraying processes is different from that obtained by hot dipping, and corrosion resistance is not always satisfactory. This is because the sprayed molten aluminum impinges upon the surface of the base metal in the form of discrete particles which have layers of aluminum oxide between them. Since the aluminum oxide is porous, the coating does not present the type of relatively solid barrier to a corrosive environment that is presented by the fused coating obtained in the hot dip process.

In general, the corrosion reaction that takes place when a metal is subjected to a corrosive environment is in the nature of a transfer of electrons from relatively anodic to relatively cathodic areas of the metal in the presence of an electrolyte. In the case of ferrous metals this results in ferrous ions going into solution in the electrolyte and there combining with oxygen or other elements. This results in the production of iron oxide, sulfide, etc.



on the surface of the metal. When a metal such as aluminum is deposited on the surface of a ferrous metal, it would naturally be expected that the aluminum would act as the anode in a corrosive reaction because aluminum is higher in the electrochemical series than ferrous metals. Consequently, when aluminum is sprayed on a ferrous metal and the coated metal exposed to a corrosive environment, the expected reaction would be a gradual corrosive wearing away of the aluminum because of a transfer of electrons to the ferrous metal, with no appreciable corrosion of the ferrous metal. However, it has been found that when aluminum is sprayed upon a ferrous metal and the coated metal subjected to industrial-type corrosive environments where oxygen and sulphur play a major role in the corrosion reaction, the aluminum to all outward appearances does not corrode at all. But upon tapping or otherwise jarring the coated ferrous metal, the aluminum coating will fall off revealing red rust and other corrosion phenomena on the surface of the ferrous metal. Thus in industrial-type environments the spray-applied coatings of pure aluminum act, for the most part, as merely physical barriers to corrosive agents. In salt containing corrosive environments, such as marine areas, on the other hand, it is known that the sprayed aluminum coatings offer corrosion protection by anodic sacrifice. These results are believed to be caused by the relatively porous nature of the sprayed coating which allows the corrosive medium to penetrate into the coating. In the industrial-type environments, the aluminum-oxide which surrounds each particle of aluminum provides a relatively corrosion resistant barrier that does not allow the corrosive environment to contact the aluminum, but instead allows uninterrupted penetration to the ferrous metal base. Thus, no anodic sacrifice is obtained. In the salt containing environments, however, the corrosive medium, generally chloride ions, quickly breaks down the oxides and attacks the aluminum. This allows anodic sacrifice to take place.

It is, therefore, an object of this invention to provide a protective aluminum coating for other metals that inhibits corrosive agents from penetrating the coating.

It is another object of this invention to provide a method of protecting metals from corrosion by increasing the anodic sacrifice of aluminum alloy coatings.

Briefly stated, in accordance with my invention, the corrosion protection afforded by a porous aluminum alloy coating deposited on other metals can be increased by adding a material to the aluminum alloy that increases its electrochemical potential.

This invention will be better understood from the following description taken in conjunction with the accompanying drawing in which:

FIG. 1 is a photomicrograph at 200× magnification showing a cross section of a coating of commercially pure aluminum sprayed on a mild steel base according to the prior art.

FIG. 2 is a photomicrograph at 200× magnification showing a cross section of a coating of aluminum and about .25% by weight lithium sprayed on a mild steel base in accordance with my invention.

FIG. 3 is a photomicrograph at 200× magnification showing a cross section of a coating of aluminum and about 1% by weight lithium sprayed on a mild steel base in accordance with my invention.

FIG. 4 is a schematic representation of the coating structure of FIG. 1.

FIG. 5 is a schematic representation of the coating structure of FIGS. 2 and 3.

Referring now to FIG. 1, therein is shown a cross section of a coating 1 of commercially pure (99.6%) aluminum that was sprayed on a base 2 of mild (1010) steel. The coating is relatively turbulent in structure and exhibits a relatively small proportion of horizontally oriented lamellar grains. This type of structure presents a relatively short means free path for the corrosive environment to the base metal because there are a great number of inter-particle boundaries oriented in the direction generally perpendicular to the base metal interlayer. This provides a relatively direct path through the coating to the base metal.

In FIGS. 2 and 3, cross sections of an aluminum alloy coating 3 containing .25% and 1% by weight lithium, respectively, are shown. FIGS. 2 and 3 show that a relatively large number of the particles in the coating are of the flat lamellar type. This means that there is a relatively long mean free path that the corrosive environment must travel from the surface of the coating to the base metal. This is caused by the relatively large number of inter-particle boundaries oriented in a direction generally parallel to the base metal interlayer. Photomicrographs of specimens coated with aluminum containing, respectively, .5% and .75% by weight lithium revealed essentially the same structure as is illustrated in FIG. 3.

FIGS. 4 and 5 are schematic representations of the coating structure of FIG. 1 and FIGS. 2 and 3, respectively. It is realized that FIGS. 4 and 5 are drastic oversimplifications of the coating structure. But, they are presented, nevertheless, to clearly illustrate the advantages of coatings having a relatively long mean free path. For a given coating thickness X, the paths C that corrosive agents must travel are relatively short in the structure of FIG. 4 because there are a relatively large number of particles A that provide inter-particle boundaries oriented in the direction of the shortest path to the base metal D. Whereas, in FIG. 5 for the same coating thickness X there are a large number of relatively flat lamellar particles B whose boundaries extend generally in a direction perpendicular to the shortest direction of travel for the corrosive environment. This results in relatively long paths C'. The consequent lengthening of the mean free path through the coating of FIG. 5 to the base metal D is believed to increase corrosion protection afforded by the coating.

I have discovered that a coating having a relatively large proportion of flat lamellar particles as illustrated in FIG. 5 can be obtained by alloying lithium with aluminum prior to spraying the coating on the base metal D. When molten droplets of the aluminum-lithium alloy are sprayed against the base metal D, the particles tend to flatten out in the direction roughly perpendicular to that at which they were sprayed. This provides a flat lamellar structure with the boundaries between adjacent particles extending roughly parallel to the surface of the base metal. When a non-lithium containing aluminum alloy is sprayed against the base metal, the droplets will not tend to flatten out as much as in the case of the aluminum-lithium alloys because the surface tension of the molten droplets of pure aluminum is greater than that of aluminum-lithium alloys. The reduction in surface tension is believed to be caused by the oxide coating around the aluminum-lithium alloy droplets being softer or less tenacious than the oxide coating around pure aluminum. Consequently, a flat lamellar structure for sprayed aluminum coatings can be obtained, according to my invention, by reducing the surface tension of the aluminum by the addition of lithium.

Aluminum-lithium alloys also provide corrosion protection for base metals that are lower than aluminum in the electrochemical series because the aluminum-



lithium alloys are more anodic. Thus aluminum-lithium alloys tend to sacrifice themselves more readily in corrosive environments than the cathode-like or nobler base metals. Since lithium is higher on the electrochemical series than aluminum, the combination of lithium and aluminum produces an alloy that is more anodic than commercially pure aluminum. This was proved when steel test specimens were first spray coated with commercially pure aluminum and then a coating of an aluminum-lithium alloy sprayed on the pure aluminum coating. Corrosive attack was resticted to the aluminum-lithium coating. When the above coatings were reversed, it was found that corrosive attack occurred at the aluminum-lithium layer with no significant attack of the base steel. Thus whether the aluminum-lithium coating was above or below the pure aluminum coating, the corrosive agents reacted with the lithium containing coating. Consequently, the addition of lithium to aluminum makes the resulting alloy more reactive, and thus the resulting alloy will provide increased cathode protection for a base metal.

The oxide coating between adjacent lamella of aluminum-lithium alloys is also believed to be less stable and more porous than the $Al_2O_3$ normally found in coatings made from commercially pure aluminum. This is believed to result in increased electrochemical contact between the coating and the surface of the base metal. The result is a greater area in which the coating can make an anodic sacrifice of electrons directly to the base metal. Also, such oxides do not offer the corrosion resistance of $Al_2O_3$ and allow the corrosive environment to penetrate to the aluminum-lithium alloy lamella or particles more quickly than it would in a coating of commercially pure aluminum. Thus, the anodic sacrifice of the aluminum-lithium alloy begins at a much earlier time than in the case of commercially pure aluminum. This inhibits penetration of the corrosive environment through the coating. This enables aluminum-lithium coatings to provide greater corrosion protection in industrial environments because delaying the penetration of the coating permits more anodic sacrifice to take place.

The foregeoing theoretical reasons for spray-applied aluminum-lithium alloys providing greater corrosion protection than coatings of commercially pure aluminum was borne out in the actual tests of samples described below.

Test specimens were prepared as follows:

A commercially obtainable 10% aluminum-lithium master alloy was melted and sufficient commercially pure (99.6%) aluminum was added to the molten master alloy to bring the percentage lithium by weight to .25%, .5%, .75%, and 1% in successive batches. The respective molten batches were cast into ingots, which were given a homogenizing heat treatment. The ingots were subsequently forged and then drawn into .125 inch wire. The wire was spray coated on the test specimens with a hand-operated Metco 4E gun in the conventional manner. The test specimens on which the coatings were deposited were low carbon (1010) steel panels, ⅛ inch x 1.5 inches x 3 inches. Each panel, just prior to being sprayed, was cleaned by blasting with No. 25 hardened steel grit. Control specimens were made by forming a wire from commercially pure 99.6% aluminum, and from commercially pure aluminum alloyed with, respectively, magnesium, silicon, beryllium, and combinations of these metals and lithium, as indicated in Table I. The latter alloys and test specimens were prepared in the same manner as described above in regard to the aluminum-lithium coated specimens. The edges of each test specimen were dipped in stop-off paint to prevent possible edge failure, and the specimens were then placed in lucite racks at an angle of 15% to the vertical. Some samples thus obtained were subjected to an accelerated industrial-type corrosion environment in a corrosion cabinet.

The results of the industrial corrosion tests are presented below in Table I.

*Table I.—Summary of Accelerated Industrial Exposure*

| Alloy | Coating thickness range (mils)[1] | Surface appearance after 60 cycles | Nature of corrosion attack |
|---|---|---|---|
| Al (commercially pure 99.6%) | 3.5-4.5 | Brown stain—white corrosion products | Some attack of base steel—failure of coating by blistering. |
| Al, 1% Mg | 4.0-4.3 | Heavy white corrosion products | Rapid surface attack of coating. |
| Al, 3% Mg | 3.8-4.5 | Heavy attack of base steel by rusting | Very rapid surface attack of coating. |
| Al, 1% Si | 4.5-5.0 | Blistering of coating—attack of base steel—red rusting. | Coating failure by attack on base steel. |
| Al, 3% Si | 3.5-4.3 | Same as above | Same as above. |
| Al, 3% Si, 0.2% Li | 4.0-4.2 | No blistering—black-grey surface | Coating intact. |
| Al, 0.5% Be | 3.7-4.2 | Coating completely corroded—red rusting | Rapid attack coating along with base steel. |
| Al, 1% Mg, 0.5% Be | 4.0-5.0 | Pinhole attack to base steel—red-brown stain—light blistering. | Failure of coating by pitting. |
| Al, 1% Mg, 0.2% Li | 4.2-4.8 | Heavy white corrosion | No attack of base steel—rapid surface attack of coating. |
| Al, 0.25% Li | 4.5-5.0 | | No attack of base steel—least attack on test specimens. |
| Al, 0.50% Li | 3.9-4.5 | Light surface attack of coating—some scattered white corrosion products—no blistering. | |
| Al, 0.75% Li | 3.6-4.3 | | |
| Al, 1.0% Li | 4.1-4.7 | | |
| Zn (commercially pure) | 4.2-4.4 | Steel base exposed with red rusting—no blistering. | Rapid surface attack and penetration of coating. |

[1] Thickness readings represent a maximum and minimum of a set of three specimen panels.

In the above described industrial corrosion exposure test, a heavy general surface attack occurred with the 1% magnesium coating, with only slight attack of the base steel. The presence of 3% magnesium produced a very rapid attack, completely destroying the coating. However, the rapid rate at which anodic sacrifice of the magnesium coatings occurred indicates that aluminum alloy coatings containing less than 1% magnesium may be commercially useable. The presence of silicon and beryllium did not improve the corrosion characteristics, and alloys containing these elements were inferior to the commercially pure aluminum. Only those coatings containing lithium showed no red rusting or staining at the end of the test period.

Because of the good corrosion protection properties obtained with the aluminum-lithium alloys, further tests were run with thinner coatings. A set of test panels identical to those described above was sprayed with a coating of aluminum and .25% lithium in the manner previously set forth. The coating thicknesses were from 1.5 to 2.5 mils. Six test specimens of this composition were exposed simultaneously with a corresponding set of specimens sprayed with commercially pure aluminum to the accelerated industrial environment, and another group of the same specimens was exposed to 20% ASTM (B-177) salt fog. After 42 cycles of industrial exposure, light attack occurred on the aluminum-lithium coatings. For a similar period of time, the pure aluminum coatings showed a heavy attack of the base steel, with initial rusting after only 8 cycles of exposure. The salt fog test also showed the superior corrosion resisting properties of the aluminum-lithium coating. Considerable rusting attack occurred in the pure aluminum coating and base steel after 1280 hours. But after 3600 hours only the surface of the aluminum-lithium coating had been attacked, as evidenced by white corrosion products. This test of specimens with relatively thin coatings shows that good corrosion protection can be obtained with coatings that are in a relatively flexible range. This test also indicates that the alteration of the oxide film and the increasing of the electrochemical potential of the alloy may be of more relative importance in obtaining corrosion protection than the greater physical barrier presented to the corrosive agents because of the increased mean free path through the coating. However, it is clear that the delaying action of the increased mean free path on corrosion penetration cooperates with the oxide breakdown and increased electrochemical potential to cause more anodic sacrifice of the coating before the base metal is attacked.

The above series of tests conclusively show that the aluminum-lithium alloy coatings provide superior corrosion protection for base metals in the alloy ranges given. From what is known about the highly reactive nature of aluminum-lithium alloys having higher percentages by weight of lithium, it is believed that commercially usable coatings cannot be prepared with lithium contents above about 3% by weight. The reason for this is that aluminum-lithium alloys containing over about 3% lithium would be so reactive that they would sacrifice themselves at a very high rate when coated on nobler metals. Thus, although the coating would offer excellent corrosion inhibiting properties while it lasted, it would corrode away so fast that it would be uneconomical because the coating would have to be renewed at frequent intervals.

Therefore, the preferred range of lithium content for aluminum alloys to provide superior corrosion inhibiting properties is from any discernable amount to about 3%. Although the samples tested were prepared from alloys having .25%, .5%, .75%, and 1% lithium by weight, respectively, it is known that the actual percentage of lithium in the spray-applied coatings was lower than the amount of lithium in the alloy as originally prepared. The reason for this is that when the aluminum-lithium alloy wire was sprayed through the coating gun, some of the lithium was vaporized when the alloy was melted and also some of the lithium combined with oxygen and other elements to form oxides. Consequently, the percentages given are the maximum percentages obtainable under the conditions described. It is believed that in the examples tested in which the sprayed wire was the .25% aluminum-lithium alloy, the actual amount of lithium in the final coating was between 1.5% and .2% by weight. As was indicated by the theories expressed previously as to why the addition of lithium to aluminum alloys increases corrosion resistance of spray-applied coatings, the addition of even a trace of lithium will increase corrosion resistance. The reasons are that any lithium will weaken the oxide and reduce the surface tension of the molten aluminum particles thus allowing them to form more flat lamella. Also, any amount of lithium will make the resulting alloy more reactive (i.e., anodic) than commercially pure aluminum.

Consequently, it has been shown that by practicing my invention, the corrosion protection afforded to base metals by spray-applied aluminum alloy coatings containing lithium is increased because the physical barrier presented to the corrosive environment increased. Also, the addition of lithium to aluminum alloys before they are sprayed upon base metals enables the coatings to provide increased cathode protection for the base metals by anodic sacrifice of the coating. These beneficial results can be obtained with coatings considerably thinner than was previously believed, and consequently articles too large to be hot-dipped can be successfully coated.

While the present invention has been described with reference to particular embodiments thereof, it will be

understood that numerous modifications may be made by those skilled in the art without actually departing from the scope of the invention. For example, the base metal employed in the samples tested was a mild steel. However, it will be obvious that other ferrous alloys, and in fact any metal nobler than the coating alloy, will receive cathodic protection when my invention is practiced. Therefore, the appended claims are intended to cover all such equivalent variations that come within the true spirit and scope of the invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of protecting metals whose major constituent is an element lower than aluminum in the electrochemical series from corrosion comprising spraying an aluminum-lithium alloy containing from a trace to about 3% by weight lithium directly on the surface of the metal.

2. The method of protecting metals whose major constituent is an element lower than aluminum in the electrochemical series from corrosion comprising spray depositing a porous lamellar structure of an aluminum-lithium alloy containing from a trace to about 3% by weight lithium in direct electrochemical contact with the surface of the metal.

3. The method of increasing the anodic sacrifice obtained from spray-applied aluminum alloy lamellar coatings for base metals whose major constituent is an element lower than aluminum in the electrochemical series in a corrosive environment comprising increasing the mean free path of the corrosive environment through the coatings by alloying from a trace to about 3% by weight lithium with the aluminum before it is sprayed upon the base metal.

4. The method of protecting ferrous metals from corrosion comprising spraying an aluminum-lithium alloy containing from a trace to about 3% by weight lithium directly on the surface of the ferrous metal.

5. The method of protecting ferrous metals from corrosion comprising spraying an alloy of aluminum and from a trace to about 3% by weight lithium directly on the surface of the ferrous metal.

6. The method of protecting ferrous metals from corrosion comprising spraying an alloy of aluminum and from about 1.5% to about 3% by weight lithium directly on the surface of the ferrous metal.

7. The method of protecting ferrous metals from corrosion comprising spraying an alloy of aluminum and from about .25% to about 1% by weight lithium directly on the surface of the ferrous metal.

8. The method of preventing the corrosion of a ferrous base metal article which is too large to be conveniently coated with a protective metal layer by dipping in a molten bath of protective metal which comprises spray coating the ferrous base metal with molten droplets of an aluminum-lithium alloy comprising over 95% aluminum and between .25% to 3% lithium whereby the lithium increases the mechanical barrier action of the coating to penetration of acid containing atmospheres by increasing the mean free path between lamellar particles of the spray applied porous coating from the outer surface thereof to its interface with the ferrous base metal and increases the anodic sacrifice action of the coating in the presence of salt containing atmospheres.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 1,988,504 | McCullough | Jan. 22, 1935 |
| 2,092,150 | Bleakley | Sept. 7, 1937 |
| 2,423,490 | Erhardt | July 8, 1947 |
| 2,711,973 | Wainer | June 28, 1955 |
| 2,782,493 | Russell | Feb. 26, 1957 |
| 2,867,546 | McNevin | Jan. 6, 1959 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 446,017 | Belgium | June 19, 1942 |