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(54) Title: A PROCESS FOR ACTIVATING A METAL SURFACE FOR CONVERSION COATING

(57) Abstract

The invention is a process for applying a phosphate coating to a metal substrate in which the metal substrate is contacted with an aqueous activating bath before the phosphate coating is applied. The improved process is obtained by applying ultrasonic vibration energy to the aqueous activating bath. The ultrasonic energy can be applied to the aqueous activating bath when the aqueous activating bath is in contact with the metal substrate or when the metal substrate is not in contact with the aqueous activating bath.

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A PROCESS FOR ACTIVATING A METAL SURFACE FOR CONVERSION COATING

Field of the Invention

The invention is an improved method for providing a phosphate conversion coating on a metal substrate.

Background of the Invention

A variety of compositions and processes have been used to provide an adherent, uniform phosphate coating on a metal surface. The phosphate coating is applied to enhance the adhesion of subsequently applied coatings and to provide for improved corrosion resistance of the coated metal substrate.

Phosphate coating processes (known as phosphating or phosphate conversion coating processes) are well known in the art. Generally, the phosphating process comprises contacting the metal surface with a acidic phosphate solution. The phosphating solution generally contains ions of metals such as zinc, nickel, manganese, copper, chromium and other metals which are known to provide conversion coatings on metal substrates in an acidic phosphate solution.

The metal substrate can be contacted with the acidic phosphate solution by immersion, spraying, roller coating, flowing and other means known for contacting a metal with an aqueous solution. Acidic phosphate conversion coating solutions are well known in the art and have been found very useful for providing a base for application of a protective coating to the metal substrate.

As disclosed in U.S. 2,310,239 to Jernstedt, US 2,874,812 to Cavanagh and Maurer and in U.S. 4,539,051, to Hacias, conversion coatings can be improved if, prior to contacting the metal to be phosphate coated with the acidic phosphate solution, the metal surface is first activated by contact with an aqueous activating composition. The aqueous activating compositions are generally mixtures comprising water with a reaction product of a titanium compound and a phosphate. The aqueous activating compositions are at an alkaline pH, generally in the range of about 7 to about 11 and preferably in the range of from about 8 to about 10. Titanium compound-phosphate compound reaction products generally contain from about 0.005 to about 25% by weight titanium. As is disclosed in the cited references, a cleaned metal substrate is contacted with an aqueous activating composition to assist in providing an even coating with low coating weight and small crystal morphology in the phosphate conversion coating step.

It is well known in the art that after the aqueous activating composition is prepared by mixing a dry activating composition with water, the aqueous activating composition loses its activating ability as time passes and the aqueous composition ages. The activating ability of the aqueous activating composition declines with time even if the composition has not been exhausted by contact with metal substrates. It would be useful to be able to extend the useful life of the aqueous activating compositions. The time period since preparation of the aqueous activating composition is known as the aging period or aging.

Contacting the metal substrate with the aqueous activating composition provides for a phosphate conversion coating which has a small crystal size, optimal coating weight and a more even coating than substrates which have been contacted with acidic phosphate solutions without prior contact with the aqueous activating composition.

Before the metal substrate is contacted with the aqueous activating composition and conversion coated, it is important that the metal substrate be clean. Cleaning of the metal substrate is generally accomplished by contacting the metal substrate with an acidic or an alkaline cleaning composition. Generally, the alkaline compositions are preferred since the activating composition is at an alkaline pH. However, as long as the metal substrate is rinsed of the cleaning solution, an acidic cleaning solution can be utilized.

A Brief Summary of the Invention

According to the present invention, an improved phosphate conversion coating can be formed on a metal substrate by the process by contacting an aqueous activating composition used to activate the metal substrate with ultrasonic vibration energy. Ultrasonic vibrations (ultrasonic energy) can be applied to the aqueous activating composition (hereinafter activating bath), in the presence or in the absence of the metal substrate which is to be activated. The largest increase in the quality of the phosphate coating in the process is obtained if the ultrasonic vibrations are applied to the activating bath in the presence of the metal substrate.

The process of the invention comprises cleaning the metal substrate, contacting the metal substrate with an activating bath which has been subjected to application of ultrasonic energy to provide an activated metal substrate and phosphating the activated metal substrate.

Brief Description of the Drawings

Figure 1 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 1 before and after aging for 12 days.

Figure 2 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 2 before and after aging for 12 days.

Figure 3 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 3 before and after aging for 12 days.

Figure 4 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 4 before and after aging for 12 days.

Figure 5 (a) and (b) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 5 before and after aging for 12 days.

Figure 6 (a), (b) and (c) are scanning electron photomicrographs of 1,000 magnification of phosphated cold rolled steel panels prepared by the process using a fresh control bath each day without ultrasonic energy applied.

Figure 7 (a), (b), (c), and (d) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 6, after aging for 1, 2, 5 and 6 days.

Figure 8 (a), (b), (c), and (d) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 7, after aging for 1, 2, 5 and 6 days.

Figure 9 (a), (b), (c), and (d) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 8, after aging for 1, 2, 5 and 6 days.

Figure 10 (a), (b), (c), and (d) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 9, after aging for 1, 2, 5 and 6 days.

Figure 11 (a), (b), (c),and (d) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 10, after aging for 1, 2, 5 and 6 days.

Figure 12 (a), (b), (c), and (d) are scanning electron photomicrographs at 1,000 magnification of phosphated cold rolled steel panels prepared by the process using Bath 11 after aging for 1, 2, 5 and 6 days.

Figure 12 (a), (b), (c) and (d) are scanning electron photomicrographs at 1,000 magnification of cold rolled steel panels phosphated on days 1, 2, 5 and 6 by the process using a freshly prepared FIXODINE® brand activating control bath each day without ultrasonic energy applied.

Figure 14 is a scanning electron photomicrograph at 1,000 magnification of a phosphated cold rolled steel panel, prepared without contact with an activating bath in the process.

Figure 15 (a), (b), (c), (d) and (e) are scanning electron photomicrographs at 1,000 magnification of the outer surface of phosphated panels of cold rolled steel (CRS), electrogalvanized steel (EG) and aluminum alloy 6061 (6061) prepared using activating Bath 11 under various conditions in the process.

Figure 16 (a), (b), (c), (d) and (e) are scanning electron photomicrographs at 1,000 magnification of the inner surface of phosphated panels of CRS, EG and 6061 prepared using activating Bath 11 under various conditions in the process.

Figure 17 (a), (b), (c), (d) and (e) are scanning electron photomicrographs at 1,000 magnification of the outer surface of phosphated panels of CRS, EG and 6061 prepared using activating Bath 12 under various conditions in the process.

Figure 18 (a), (b), (c), (d) and (e) are scanning electron photomicrographs at 1,000 magnification of the inner surface of phosphated panels of CRS, EG and 6061 prepared using activating Bath 12 under various conditions in the process.

Figure 19 (a), (b), (c), (d) and (e) are scanning electron photomicrographs at 1,000 magnification of the outer surface of phosphated panels of CRS, EG and 6061 prepared using activating Bath 13 under various conditions in the process.

Figure 20 (a), (b), (c), (d) and (e) are scanning electron photomicrographs at 1,000 magnification of the inner surface of phosphated panels of CRS, EG and 6061 prepared using activating Bath 13 under various conditions in the process.

Figure 21 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of the outer phosphated surface of metal panels prepared using a freshly prepared control bath in the process.

Figure 22 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of the inner phosphated surface of metal panels prepared using a freshly prepared control bath in the process.

Figure 23 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels (a) CRS, (b) EG and (c) 6061 prepared using stirred Bath 14 (for comparison) in the process.

Figure 24 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels (a) CRS, (b) EG and (c) 6061 prepared by the process by applying ultrasonic energy to Bath 15 while the metal panels were immersed in the bath.

Figure 25 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels (a) CRS, (b) EG and (c) 6061 prepared using Bath 15 five minutes after stopping application of ultrasonic energy to the bath in the process.

Figure 26 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels prepared using stirred Bath 16 in the process (for comparison).

Figure 27 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels prepared by the process by applying ultrasonic energy to Bath 17 while the metal panels were immersed in the bath.

Figure 28 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels prepared by the process wherein the metal panels are immersed in Bath 17 five minutes after the ultrasonic vibrations were discontinued.

Figure 29 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels prepared using stirred Bath 18 in the process (for comparison).

Figure 30 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels prepared by the process by immersing the panels in Bath 19 while ultrasonic energy was applied to Bath 19.

Figure 31 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of phosphated metal panels prepared by the process by immersing the panels in Bath 19 five minutes after the application of ultrasonic energy to the bath was stopped.

Figure 32 (a), (b), and (c) are scanning electron photomicrographs of phosphated metal panels prepared by the process using a freshly prepared control bath.

Description of the Preferred Embodiments of the Invention

Metal substrates which can be advantageously treated by the process of the present invention include iron, zinc, zinc alloys, aluminum and aluminum alloys containing at least about 60%-70% aluminum. The substrate to be treated by the process of the present invention need not be made of the metal alone. That is, zinc plated and aluminum composite materials may be advantageously treated by the process of the invention.

As is well known in the art for providing phosphate coatings on metal substrates, the metal must be clean to permit an adherent phosphate coating to be formed. The metal substrates are generally cleaned by contact with an alkaline or an acid cleaning solution to remove any grease, dirt, scale, oxidized coating and the like from the surface of the metal substrate. Acid cleaners generally contain sulfuric and/or phosphoric acid. In addition, if the metal substrate is aluminum, a small amount of fluoride ion is generally included in the cleaning composition.

Alkaline cleaners can be utilized to prepare the metal substrate for accepting the phosphate coating. Alkaline cleaners are generally composed of alkali materials such as caustic, soda ash, trisodium phosphate, sodium polyphosphate, sodium silicate, and surfactants. The metal substrate to be cleaned is contacted with a dilute solution of the alkaline cleaner. The metal to be cleaned is generally contacted with the aqueous cleaning solution at a temperature in the range of from about ambient to about 160°F and preferably from about 100°F to about 150°F. Metal can be cleaned by contacting the metal with the aqueous cleaning composition by immersion, spraying, flowing, and other means for contacting a metal with an aqueous cleaning solution. Generally, the metal substrate is immersed in the aqueous solution or the aqueous cleaning solution is sprayed onto the metal substrate. The metal is contacted with the cleaning solution for from about 30 seconds to about 10 minutes and preferably from about 1 to about 3 minutes.

After the metal substrate has been cleaned with the cleaning solution, the cleaning solution is rinsed from the surface of the metal substrate with water.

After the metal substrate has been cleaned and rinsed with water, the metal substrate is generally contacted with a mixture of water and an activating composition. A preferred activating composition is a reaction product of a titanium compound with a phosphate compound. The activating compositions are mixed with the water to form an aqueous activating composition (activating bath) and contacted with the metal substrates. Preferably, the aqueous activating composition contains from about 0.05 to about 25 grams per liter of the activating composition. The activating composition is generally not soluble in water and a dispersion of the activating composition in an aqueous phase (activating bath) is generally obtained.

The activating composition is a reaction product of a titanium containing composition with a phosphate. This reaction product can be combined with an additional phosphate material such as sodium tripolyphosphate, sodium pyrophosphate, disodium phosphate and the like. The activating composition is a dry material containing at least 0.005% titanium and is mixed with water to form the aqueous activating composition. The activating composition may contain an alkaline material such as sodium carbonate or caustic to help provide an aqueous activating composition with an alkaline pH. The pH is generally between about 7 and 11 and preferably between about 8 and 10.

In known processes, the cleaned metal substrate is then contacted with the activating bath for from about 5 seconds to about 10 minutes, preferably from about 20 seconds to about 5 minutes. The activating bath is contacted with the metal substrate at a temperature of from about ambient to about 150°F, preferably from about 75 to about 110°F.

Applicants have discovered that if ultrasonic vibrations (ultrasonic energy) are applied to the activating bath, a phosphate conversion coating, which is later formed on the substrate, has a smaller crystal size, an optimum coating weight and is more uniform. That is, the surface of the metal substrate is more uniformly coated with a phosphate coating. The ultrasonic power can be applied to the aqueous activating composition alone or it can be applied to the aqueous activating composition when in contact with a metal surface which is to be activated. The most dramatic results are provided when the ultrasonic power is applied to the aqueous activating composition when in contact with the metal substrate to be activated. Ultrasonic power can be applied to the aqueous activating composition in the metal contacting zone in the presence or absence of a metal substrate or can be applied to the aqueous activating composition in a separate ultrasonic treating zone outside of the contacting zone. The ultrasonic power can be applied to the aqueous activating composition continuously, only when the aqueous activating composition is being used to activate a metal substrate, only when the aqueous activating composition is not being used to contact metal substrate, in a predetermined discontinuous manner or in a discontinuous random manner. In a preferred embodiment, the metal substrate is contacted with the aqueous activating composition at the same time as ultrasonic power is applied to the composition.

The metal substrate can be contacted with the aqueous activating composition by immersion, spraying, flowing or any other method used for contacting a metal substrate with an aqueous composition.

Applicants have discovered that the aqueous activating composition has a lesser improvement on the final phosphate coating when the ultrasonic power is applied to the aqueous activating composition in the absence of the metal substrate or applied to the aqueous activating composition externally to the contact zone. Excellent phosphate coatings are formed on the metal substrate when the ultrasonic power is applied to the aqueous activating composition in a contacting zone during contact with the metal substrate to be activated.

After the metal substrate has been removed from contact with the activating bath, the metal substrate is then passed to a phosphate conversion coating zone. In the phosphate conversion coating zone, the activated metal substrate is contacted with an acidic phosphate containing conversion coating solution to provide an adherent metal phosphate coating on the metal substrate.

Phosphate conversion coating compositions are well known to one skilled in the art. Phosphate conversion coating compositions have been used for more than 40 years. The acidic phosphate compositions are well known; however, new additives to increase the rate at which the coating is formed, alter the size and shape of the crystals of the coating and the like can be included in the composition to provide a more useful coating.

As is well known in the art, the goal of a phosphate conversion coating process is to provide an adherent coating with a crystal structure optimized for the intended use, with maximum coverage for the weight of phosphate coating. Clearly, when the phosphate coating is to be coated with an additional organic coating material, to form a corrosion resistant coating, the phosphate coating is desirably as even as possible and of the lowest weight per unit area. Uniform coatings of small crystal size and excellent coverage can be provided by the process of the present invention.

In the phosphating process, contact with the activating bath is required to provide a uniform coating having crystals with a small size. After the substrate has received the phosphate coating, the substrate is then rinsed to remove the acid phosphate solution.

The phosphate coating can be further improved by contacting the phosphate coated metal with a sealing and adhesion promoting composition. Generally, the sealing and adhesion promoting composition is an acidic chromate containing solution. However, other post treatment solutions can be utilized. The phosphated metal can be coated by additional coating materials known in the art.

A series of experiments were conducted to determine the effect of ultrasonic vibrations on the properties of phosphate coatings prepared by contacting a cleaned metal substrate, to be phosphate coated, with a titanium compound-phosphate reaction product activating composition in an aqueous dispersion.

Experiment 1

Metal test panels were processed using a standard phosphating process cycle. In the tests, the metal test panels were treated according to the following process. The metal test panels were cleaned by contact with PARCO® CLEANER 1500C at 2 ounces per gallon at 110°F by spraying for 2 minutes; rinsing with warm water with a 45 second spray; contact with an aqueous activating composition of water and FIXODINE® ZN at 80°F by immersion for 30 seconds; contact with a BONDERITE® 3080 phosphating solution according to manufacturers' recommendations, by immersion in the aqueous phosphating solution at 112°F for 2 minutes. After immersion in the phosphate coating composition, the panels were rinsed with cold water for 30 seconds and oven dried.

PARCO® CLEANER 1500C is an alkali cleaner (product of Parker+Amchem). FIXODINE® ZN activating composition is a composition containing a reaction product of a titanium containing compound with phosphates, subsequently mixed with sodium phosphates and sodium carbonate (product of Parker+Amchem). BONDERITE® 3080 phosphating composition is an aqueous acidic zinc-manganese-nickel-phosphate conversion coating composition (product of Parker+Amchem).

The effect of ultrasonic power applied to the aqueous activating composition on the phosphate coatings formed by the process were determined by the following experimental design.

	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5
Day 1	*X	US*X	US*X	US*X	*X
Day 2	-	-	-	US*	-
Day 3	*	*	*	US*	*
Day 4	-	-	-	US*	-
Day 5	*	*	US*	US*	*
Day 8	*	*	*	US*	*
Day 9	-	-	-	US*	-
Day 10	*	*	US*	US*	*
Day 11	-	-	-	US*	-
Day 12	*X	*X	*X	*X	*X
Day 12	US*X	US*X	US*X	US*X	-

*	Bath conditions and particle size were checked.
US	Ultrasonic vibration applied to activating bath.
X	Test panel contacted with the aqueous activating bath.
-	No tests or treatments to the activating bath.

A standard water solution was prepared by diluting

79 ml $CaCl_2$ solution (10 g/l)
53 ml $MgSO_4$ solution (10 g/l)
26 ml $NaHCO_3$ solution (10 g/l)

to 9 liters with deionized water. This solution is noted as standard water and was utilized to prepare the FIXODINE® ZN brand activating baths. The standard water was analyzed and found to contain: 21 ppm Ca, 10 ppm Mg, 7 ppm Na and hardness (as $CaCO_3$) of 120 ppm.

Activating Baths 1-4 were prepared by mixing 1.5 grams of FIXODINE® ZN brand activating composition and 0.22 grams of soda ash (for adjustment of pH 9.0±0.3) per liter of standard water.

Bath 5 was prepared by mixing 1.5 grams of FIXODINE® ZN brand activating composition and 0.22 grams of soda ash (pH adjustment to 9.0±0.3) per liter of deionized water.

No ultrasonic vibrations were applied to activating Baths 1 and 5. Ultrasonic vibrations at a frequency of 40 kilohertz were applied to activating Baths 2, 3 and 4 for 2 minutes. In addition the baths were treated with ultrasonic vibration as shown in the experimental design.

All the baths were analyzed for total titanium, filterable titanium, pH and total alkalinity.

Total titanium is the total amount of titanium in the activating bath in parts per million.

Filterable titanium is the amount of titanium, in parts per million, in the activating bath which passes through a filter medium with 2.5 micron openings.

Total alkalinity is determined as the number of ml of 0.1N H_2SO_4 required to titrate a 10 ml sample to a bromphenol blue end point.

The test panels were prepared after ultrasonic vibrations had been applied to the activating baths in accordance with the experimental design. The ultrasonic vibrations were applied to the activating baths in the ultrasonic power zone of a BRANSONIC® Model PC620 at 40 kilohertz in all experiments reported in this application.

Test panels were prepared by the process on day 1 after ultrasonic treatment of the activating bath (if applicable) and on day 12 before and after ultrasonic treatment of the activating bath. The ultrasonic treatment of the activating Baths 1 through 4 was in the treating zones in the absence of the metal substrate. The results of the test are set forth in Tables 1 through 5. Tables 1 through 5 disclose the properties of the bath and in addition provide coating weight, crystal size and crystal number.

The crystal number is the number of crystals in one square inch of the scanning electron photomicrograph at 1,000 magnification of the surface of the coated substrate. The maximum crystal number reported is 100. This includes metal substrates wherein there are more than 100+ crystals per square inch in the scanning electron photomicrograph at 1,000 magnification of the coated metal surface. The preferred coatings have an optimum coating weight, small crystal size and a large crystal number.

The data in Tables 1-5 show that ultrasonic energy treatment of aged activating baths, when not in contact with the metal substrate, provides a lower coating weight with a smaller crystal size and a larger crystal number than aged aqueous activating baths which have not been ultrasonically treated. The best phosphate coatings after 12 days aging of the bath were obtained by using activating baths which had been treated with ultrasonic vibrations every day during the 12 days of aging. The coating weight after 12 days aging was the same as the coating weight of phosphate coating obtained by using the fresh activating bath in the process, with the same crystal size and nearly the same crystal number.

Activating Bath 5 was prepared with deionized water. It is generally known that the activating effect of the activating bath made with deionized water deteriorates during aging. Bath 5 was included in this study to show that the effect of the application of ultrasonic energy to the Baths 1 through 4 was different than the effect seen with deionized water. With the application of ultrasonic energy to the activating bath, excellent coatings were obtained, even after aging of the baths.

TABLE 1 - BATH 1

	Ultrasonics Applied	Total Ti (ppm)	Filterable Ti (ppm)	pH	Total Alkali (points)	Coating Weight (g / sq m)	Crystal Size (microns)	Crystal Number
Day 1	no	16.0	3.0	9.10	3.4	2.33	1 – 4	100
Day 2	no							
Day 3	no	16.0	4.5	8.91	3.5			
Day 4	no							
Day 5	no	16.0	4.0	8.86	3.4			
Day 8	no	16.0	4.0	8.80	3.3			
Day 9	no							
Day 10	no	9.0	3.0	8.73	3.5			
Day 11	no							
Day 12	no	15.5	3.0	8.74	3.3	3.27	3 – 8	30
Day 12	yes	11.0	6.0	8.78	3.4	2.36	1 – 5	65

TABLE 2 - BATH 2

	Ultrasonics Applied	Total Ti (ppm)	Filterable Ti (ppm)	pH	Total Alkali (points)	Coating Weight (g / sq m)	Crystal Size (microns)	Crystal Number
Day 1	yes	16	6.0	9.15	3.4	2.12	1 – 3	100
Day 2	no							
Day 3	no	16	4.5	9.07	3.5			
Day 4	no							
Day 5	no	16	7.0	8.98	3.4			
Day 8	no	16	6.0	8.91	3.4			
Day 9	no							
Day 10	no	12	2.0	8.83	3.8			
Day 11	no							
Day 12	no	14	4.0	8.80	3.5	3.22	3 – 8	35
Day 12	yes	13	6.0	8.75	3.5	2.22	1 – 4	85

TABLE 3 - BATH 3

	Ultrasonics Applied	Total Ti (ppm)	Filterable Ti (ppm)	pH	Total Alkali (points)	Coating Weight (g / sq m)	Crystal Size (microns)	Crystal Number
Day 1	yes	16	8	8.98	3.35	2.17	1 – 4	100
Day 2	no							
Day 3	no	16	5	8.91	3.50			
Day 4	no							
Day 5	yes	16	8	8.85	3.50			
Day 8	no	16	6	8.79	3.40			
Day 9	no							
Day 10	yes	11	7	8.74	3.50			
Day 11	no	12	6	8.73	3.50			
Day 12	no	15	7	8.72	3.40	2.55	2 – 5	60
Day 12	yes	12	6	8.80	3.40	2.34	1 – 4	75

TABLE 4 - BATH 4

	Ultrasonics Applied	Total Ti (ppm)	Filterable Ti (ppm)	pH	Total Alkali (points)	Coating Weight (g / sq m)	Crystal Size (microns)	Crystal Number
Day 1	yes	17	5	8.95	3.35	2.24	1 – 4	100
Day 2	yes	17	7	8.89	3.30			
Day 3	yes	17	11	8.84	3.40			
Day 4	yes	16	9	8.81	3.40			
Day 5	yes	16	10	8.78	3.50			
Day 8	yes	16	8	8.73	3.40			
Day 9	yes	16	8	8.73	3.40			
Day 10	yes	14	7	8.68	3.90			
Day 11	yes	14	11	8.69	3.90			
Day 12	no	16	7	8.67	3.30	2.59	2 – 5	60
Day 12	yes	15	8	8.70	3.40	2.30	1 – 4	90

TABLE 5 - BATH 5

	Ultrasonics Applied	Total Ti (ppm)	Filterable (ppm)	pH	Total Alkali (points)	Coating Weight (g / sq m)	Crystal Size (microns)	Crystal Number
Day 1	no	16	16	8.97	3.1	2.33	2 – 6	60
Day 2	no							
Day 3	no	16	15	8.95	3.1			
Day 4	no							
Day 5	no	16	16	8.90	3.1			
Day 8	no	16	16	8.83	3.2			
Day 9	no							
Day 10	no	14	12	8.76	3.5			
Day 11	no							
Day 12	no	16	16	8.75	3.1	3.98	10 – 40	2

Figures 1 through 6 are scanning electron photomicrographs, at a magnification of 1,000, of phosphate coated cold rolled steel panels. The phosphate coating was applied to cold rolled steel panels which had been activated with activating baths according to the experimental design. It is clear from an examination of the figures, and in particular, a comparison of Figures 5 and 1 with Figures 2 through 4 that the ultrasonic treatment of the activating bath substantially improves the phosphate coating which is formed on the metal substrate by the process.

As shown in Tables 1 through 5 and Figures 1 through 6, as the activating bath ages, its effectiveness for promoting the rapid formation of a high quality phosphate coating having a small crystal size and high crystal number decreases. Subjecting the activating bath to ultrasonic vibrations increases the usefulness of the activating bath for promoting a satisfactory phosphate conversion coating during the phosphating step of the process.

<u>Experiment 2</u>

A series of experiments was carried out to determine the effect of water hardness on the activating ability of the activating baths. The series of experiments disclosed that water hardness can have a deleterious effect on the ability of the activating bath to promote the formation of high quality, small crystal size phosphate coatings on metal substrates. The characterizations of the activating baths are shown in Table 6.

TABLE 6

BATH	ACTIVATING BATH	CONCEN-TRATION	Mg2+ PPM	Ca2+ PPM	SONICATED	TOTAL Ti PPM
6	PARCOLENE® Z	1.2 g/L	0	0	NO	17
7	PARCOLENE® Z	1.2 g/L	0	0	YES	16
8	PARCOLENE® Z	1.2 g/L	2	4	NO	18
9	PARCOLENE® Z	1.2 g/L	2	4	YES	16
10	PARCOLENE® Z	1.2 g/L	6	8	NO	15
11	PARCOLENE® Z	1.2 g/L	6	8	YES	14
CONTROL	FIXODINE® Z8	1.5 g/L			NO	16

PARCOLENE® Z contains the same titanium compound-phosphate compound reaction product as FIXODINE® Z8 but does not contain condensed phosphate

The test panels were coated according to the following procedure.

STEP	MATERIAL	TEMPERATURE	TIME	APPLICATION METHOD
Clean	[1]PARCO® CLEANER 1500C 2 oz per gal.	120°F	120 seconds	spray
Rinse	water	100°F	60 seconds	spray
Activation	[2]PARCOLENE® Z or FIXODINE® Z8	90-100°F	30 seconds	immersion or spray
Conversion Coating	[3]BONDERITE® 958 according to manuf. recommendations	120-130°F	120 seconds	immersion
Rinse		cold water	60 seconds	spray
Rinse	deionized water		30 seconds	spray
Oven Dry		225°F	5 minutes	

[1] PARCO® CLEANER 1500C	Alkaline cleaner (Product of Parker+Amchem)
[2] PARCOLENE® Z	Titanium compound-phosphate compound reaction product with added phosphates. Does not contain condensed phosphate. (Product of Parker+Amchem)
[3] FIXODINE® Z8	Titanium compound-phosphate compound reaction product containing condensed phosphates. (Product of Parker+Amchem)
BONDERITE® 958	A commercial acidic zinc-nickel-manganese phosphate conversion coating composition (Product of Parker+Amchem) used according to manufacturers' recommendations

Table 6 shows the parameters of the activating baths. The content of titanium was adjusted to be approximately the same in all the baths. The amount of magnesium and calcium in the aqueous activating bath is shown in Table 6. In addition, application of ultrasonic energy to the activating bath is also shown in Table 6. The ultrasonic energy was applied to the baths in the absence of the metal substrate. Table 7 sets forth the coating weight, the crystal size and the coverage of the phosphate coating on the activated metal substrate provided by the process. The Coating Ratings 1 through 6 utilized in Table 7 and other tables in the specification are as follows: Ratings of 1-3 were given to panels which showed a continuous coating at 1,000 times magnification. A rating of 1 indicates small crystal size morphology, a rating of 3 indicates poor (large) crystal size morphology. Ratings of 4-6 were given if any discontinuinties were observed in the coating at 1,000 times magnification. A rating of 4 indicates a coating with low coating weight and small crystal size, but with surface areas void of phosphate coating. A rating 6 indicates poor surface coverage and large crystal size.

TABLE 7

BATH 6	DAY 1	DAY 2	DAY 5	DAY 6	DAY 13
COATING WEIGHT	279	275	421	457	
CRYSTAL SIZE	2-10	2-8	5-15	5-21	
COVERAGE RATING	1	1	1	1	
FILTERABLE Ti	10	11	2	0	
BATH 7					
COATING WEIGHT	231	221	212	197	
CRYSTAL SIZE	2-5	1-5	1-3	2-4	
COVERAGE RATING	1	1	1	1	
FILTERABLE Ti	10	12	12	12	
BATH 8					
COATING WEIGHT	557	318	362	331	
CRYSTAL SIZE	5-40	20-60	20-60	9-65	
COVERAGE RATING	4	6	6	6	
FILTERABLE Ti	0	0	0	0	
BATH 9					
COATING WEIGHT	566	464	438	443	
CRYSTAL SIZE	5-40	3-40	5-30	2-25	
COVERAGE RATING	4	5	5	4	
FILTERABLE Ti	0	0	0	0	
BATH 10					
COATING WEIGHT	564	343	391	487	246

TABLE 7 (continued)

BATH 10	DAY 1	DAY 2	DAY 5	DAY 6	DAY 13
CRYSTAL SIZE	6-20	20-55	20-55	9-63	7-49
COVERAGE RATING	3	6	6	6	5
FILTERABLE Ti	0	5	5	0	
BATH 11					
COATING WEIGHT	593	488	451	487	405
CRYSTAL SIZE	5-40	6-40	7-35	7-29	4-25
COVERAGE RATING	3	5	5	5	3
FILTERABLE Ti	5	0	0	0	
CONTROL					
COATING WEIGHT	304	212	218	177	195
CRYSTAL SIZE	2-5	1-7	1-5	1-3	1-3
COVERAGE RATING	1	1	1	1	1

Coating weight - milligrams per square foot
Crystal size - microns

A study of the results of Baths 6 and 7, on days 1 and 2, as reported in Table 7 shows that a good coating with small crystal size and optimal coating weight was obtained with a fresh activating bath prepared from PARCOLENE® Z with deionized water.

Bath 7 is a sonicated bath with the same composition as Bath 6. As shown in Table 7, use of Bath 6 as an activating bath in the process provided a good coating when fresh, but did not provide suitable coatings on days 5 and 6. The crystal size substantially increased with a concurrent increase in coating weight. The coating weight, crystal size and coverage of the phosphate coating when prepared by the process which utilizes the sonicated activating Bath 7 was equivalent, even after aging, to that provided by the control, which was a fresh activating bath prepared every day and applied by spraying onto the cold rolled steel panel.

Table 7 also shows that the magnesium and calcium hardness in the water used to prepare the activating bath affected the ability of the bath to promote an optimal coating on the cold rolled steel panel. The loss of coating quality can be seen by the results reported as Baths 8, 9, 10 and 11. The ultrasonically treated Baths 9 and 11 promoted slightly better phosphate coatings than Baths 8 and 10 which were not ultrasonically treated. After one day aging the coatings were not satisfactory. Scanning electron photomicrographs at 1,000 times magnification of the phosphate coatings produced by use of activating Baths 6 through 11 and the Control Bath are shown in Figures 7 through 13 respectively. Figure 14 is a scanning electron photomicrograph at 1,000 magnification of a phosphate coating produced on a non-activated cold rolled steel surface.

A study of Figures 7 through 14 clearly illustrates the effect of application of ultrasonic energy to the activating bath on the phosphate coating of the metal substrate produced by the process.

Table 7 also shows the characteristics of phosphate coatings produced by the process using activating Baths 10 and 11 after aging for 13 days; using the same procedure as for the previous examples (Bath 11, sonicated in the absence of the metal substrate). The phosphate coatings produced by the process using the activating Baths 10 and 11 aged for 13 days were not satisfactory.

An additional experiment was carried out using Bath 11 aged 13 days, but applying ultrasonic energy to the activating bath while it was contacting the metal panel being activated. Unexpectedly, the phosphated conversion coating produced on the activated panel was of excellent quality. A similar experiment was carried out using Bath 11 after aging for 150 days. Cold rolled steel, electrogalvanized steel and aluminum panels were processed. When ultrasonic energy was applied to Bath 11 after 150 days aging, when the bath was in contact with the metal panels, the phosphate coatings formed on the activated panels were excellent on all substrates. The phosphate coating was comparable to the phosphate obtained by the process by using the freshly prepared control activating bath.

In view of the excellent phosphate coatings which are obtained when the ultrasonic vibrations are applied to the aqueous activating bath in contact with the metal substrate to be activated, additional experiments were carried out to determine the effectiveness of the treatment.

It is not completely clear whether the improvement in the phosphate coating obtained by the process, when ultrasonic energy is applied to the activating bath in the presence of the metal substrate, is due solely to an optimization of the size of the particles of the activating bath during sonication, or whether an element of the improvement is due to an interaction between the ultrasonic vibrations and the metal substrate.

Experiment 3

In many applications where a phosphate coating is desired, the parts to be coated are irregularly shaped with recessed or boxed areas. These recessed areas are more difficult to coat with a high quality phosphate coating. A series of experiments were carried out to determine the effect of ultrasonic energy application during the phosphate coating process, when the surface of the substrate is not directly exposed to the ultrasonic vibrations. Four inch by six inch metal panels were inserted into a plastic frame to form a box in which the internal surfaces of the box were not directly exposed to the ultrasonic vibrations. The two panels inserted in the plastic frame were separated by 5/8th of an inch between the panels. The top and bottom of the box contained holes which allowed the activating bath to fill the box while hindering the circulation of the activating solution in the box. The coatings formed on the panels were rated according to the method set forth (1-6).

Both the panel surfaces which formed the outside of the box and the panel surfaces which formed the inside of the box were examined for phosphate coating characteristics and rated. The 150 day old PARCOLENE® Z Bath 11 was included in the study since 150 day old Bath 11, when ultrasonic energy was applied during activation in the contact zone, provided a metal substrate with an excellent phosphate coating. In addition, activating baths with reduced amounts of titanium were prepared and tested as the activating bath in the process.

The compositions of the baths are set forth in Table 8.

TABLE 8

BATH	CONDITIONER	CONCENTRATION	Mg^{2+} PPM	Ca^{2+} PPM	SONICATED	TOTAL Ti PPM
11	PARCOLENE® Z	1.2 g/L	6	8	YES	14
12	PARCOLENE® Z	0.37 g/L	6	8	YES	5
13	PARCOLENE® Z	0.37 g/L	11	22	YES	5
CONTROL	FIXODINE® Z8	1.5 g/L	11	22	NO	16

Figures 15 and 16 are scanning electron photomicrographs, at a 1,000 times magnification, of the phosphated side of the panel which was the the outer surface of the box and the side of the phosphated panel which formed the inner surface of the box which were treated by aqueous activiting Bath 11. The various treatments are noted as a, b, c, d, and e in Figure 15 and Figure 16. Figures 15 and 16 clearly show the improvement in the phosphate coating on both the inner and outer surfaces when ultrasonic vibrations are applied to the activating bath when it is in contact with the metal substrate in the process of the invention. Table 9 presents the crystal size and coverage of the phosphate coating when applied to cold rolled steel, galvanized steel and aluminum alloy 6061 by the process of the invention when ultrasonic energy is applied to the activating baths, as set forth in Table 8, when the baths are in contact with the box formed from the metal panels.

TABLE 9

	SONICATE	CRS		EG		6061	
		outside	inside	outside	inside	outside	inside
BATH 11							
CRYSTAL SIZE	NO			5-12	10-40	4-12	20-30
COVERAGE RATING	NO			2	3	4	5
CRYSTAL SIZE	YES	3 - 15	3 - 8	3 - 7	3 - 6	5 -20	5 - 12
COVERAGE RATING	YES	2	4	1	1	2	4
BATH 12							
CRYSTAL SIZE	NO	4 - 15	3 - 12				
COVERAGE RATING	NO	2	4				
CRYSTAL SIZE	YES	2 - 7	3 - 7	3 - 7	3 - 7	4 - 10	3 - 6
COVERAGE RATING	YES	1	4	1	2	1	2
BATH 13							
CRYSTAL SIZE	NO	5 - 20	4 - 15				
COVERAGE RATING	NO	3	5				
CRYSTAL SIZE	YES	2 - 12	4 - 6	2 - 8	2 - 8	3 - 10	4 - 10
COVERAGE RATING	YES	2	4	1	1	1	2
CONTROL							
CRYSTAL SIZE	NO	2 -6	1 - 3	2 - 8	2 - 5	3 - 8	2 - 7
COVERAGE RATING	1	1	1	1	1	1	1

Crystal size - microns

The phosphate coatings formed by the process are improved. The surfaces of the metal panels which faced the interior of the box also showed improvement in the phosphate conversion coating. In all cases in which ultrasonics were applied, coating coverage and crystal size on an electrogalvanized steel on both the inner and outer panel surfaces was excellent. The effect of the 150 day old activating Bath 11 without application of ultrasonic vibrations (stirred) is shown for comparison. The inner and outer panel surfaces of aluminum phosphated after treatment with activating Bath 11 showed a significant improvement due to application of ultrasonic vibration when in contact with the metal substrate. The inner surface is almost completely covered with a phosphate coating with application of ultrasonic energy while it is almost completely bare when treated with the activating bath without application of ultrasonic energy. The outer surfaces of the CRS were completely phosphate coated when activated by the 150 day old Bath 11 with application of ultrasonic energy. The inner surfaces of the CRS showed incomplete coating but the coating is significantly better than the coating formed when processed with Bath 10 after only 1 day aging (Figure 11(b)).

Baths 12 and 13 which contained a reduced amount of the activating composition (low titanium level) also showed improved phosphated coating when ultrasonic energy was applied to the activating bath when the bath was in contact with the metal substrates.

Figures 17 and 18 are scanning electron photomicrographs at 1,000 magnification of the outer surface and the inner surface of the metal panels prepared by the process of the invention utilizing Bath 12 with the reduced content of activating composition. A comparison of Figure 17 and 18 (a) and (b) clearly shows the improvement when ultrasonic energy is applied to the activating bath when the bath is in contact with the metal substrate. The inner and outer surfaces of the panels show improved phosphate coating. Figures 17 and 18 (c) and (d) show the effect of application of ultrasonic energy to the activiting bath on the coating of electrogalvanized steel and aluminum alloy 6061.

Figures 19 and 20 are scanning electron photomicrographs at 1,000 magnification of the outer and inner surfaces of metal panels treated with activating Bath 13. It is clear from a comparison of Figure 19 and Figure 20 (a) and (b) that application of ultrasonic energy to the bath while the metal substrate is immersed in the bath substantially improves the crystal size and coverage obtained in the phosphate coating formed by the process of the invention.

Figures 21 and 22 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of the outer and the inner surfaces of panels formed from cold rolled steel, galvanized steel and aluminum alloy 6061 using a freshly prepared control bath for activation.

Figures 15, 16, 17, 18, 19 and 20 illustrate that the application of ultrasonic energy to the aqueous activating bath in the presence of the metal substrate to be activated comprises a significant improvement in the activation of both the exposed and recessed surfaces. The figures also indicate that the concentration of the activating composition in the activating bath can be reduced if ultrasonic energy is applied to the activating bath while the metal substrate is in contact with the activating bath.

<u>Experiment 4</u>

Tests were run to determine the effect of application of ultrasonic energy to FIXODINE® Z8 aqueous activating baths. Treatment Baths 14, 15, 16, 17, 18 and 19 were prepared. Baths 14, 15, 16, and 17 utilized various concentrations of FIXODINE® Z8 and were prepared utilizing tap water. Baths 18 and 19 were prepared with PARCOLENE® Z at a low concentration utilizing tap water.

The compositions of the baths and the treatments are set out in Table 10.

TABLE 10

BATH	CONDITIONER	CONCENTRATION	WATER	SONICATED	TOTAL Ti PPM
14	FIXODINE® Z8	1.5 g/L	Tap	NO	16
15	FIXODINE® Z8	1.5 g/L	Tap	YES	17
16	FIXODINE® Z8	0.5 g/L	Tap	NO	5
17	FIXODINE® Z8	0.5 g/L	Tap	YES	4
18	PARCOLENE® Z	0.4 g/L	Tap	NO	6
19	PARCOLENE® Z	0.4 g/L	Tap	YES	6
CONTROL	FIXODINE® Z8	1.5 g/L	Tap	NO	16

All cold rolled steel panels treated with the fresh FIXODINE® Baths 14 through 17 and the control bath produced good phosphate coatings with or without application of ultrasonic power to the activating baths. The PARCOLENE® Z activating bath did not provide a good coating when the fresh solution was stirred. When ultrasonic energy was applied to Bath 19 while in contact with the metal substrate to activate the substrate, the phosphate coating produced by the process was satisfactory. The characteristics of the phosphate coatings are shown in Table 11.

TABLE 11

	BATH 14	BATH 15	BATH 16	BATH 17	BATH 18	CONTROL
SONICATE	NO	YES	NO	YES	NO	NO
COATING WEIGHT	219	195	312	276	369	207
CRYSTAL SIZE	1-4	1-5	3-12	2-10	20-40	1-5
COVERAGE RATING	1	1	1	1	6	1

Coating weight - milligrams/Ft.^{2}
Crystal size - microns

The activating Baths 14-19 were then aged for 90 days and used to treat cold rolled steel, electrogalvanized steel, and aluminum alloy 6061. In all cases when ultrasonic vibration energy was applied to the activating baths (Bath 14-19) while the baths were in contact with the metal substrate, the phosphated coatings were good. The results of the tests are shown in Table 12.

TABLE 12

	Sonication	Filterable Ti	CRS	EG	6061
BATH 14	none	9			
Coating Weight			354	411	315
Crystal Size			4 - 10	3 - 11	2 -13
Coverage Rating			2	1	4
BATH 15	yes	4			
Coating Weight	on off		222 246	312 321	282 279
Crystal Size	on off		2 - 4 2 - 4	2 - 7 2 - 6	2 - 12 2 - 14
Coverage Rating	on off		1 1	1 1	1 1
BATH 16	none	0			

TABLE 12 (continued)

	Sonica-cation	Filter-able TI	CRS	EG	6061
Coating weight			519	531	252
Crystal size			15 - 40	3 - 8	10 - 25
Coverage Rating			6	1	6
BATH 17	yes	0			
Coating Weight	on off		243 345	378 423	285 309
Crystal Size	on off		1 - 4 3 - 10	3 - 8 3 - 12	2 - 13 4 - 20
Coverage Rating	on off		1 2	1 2	4 4
BATH 18	none	0			
Coating Weight			543	519	294
Crystal Size			20 - 70	7 - 20	10 - 25
Coverage Rating			6	3	6
BATH 19	yes	0			
Coating Weight	on off		381 588	411 456	345 294
Crystal Size	on off		3 - 8 10 - 50	2 - 8 3 - 10	3 - 20 15 - 30
Coverage Rating	on off		2 6	1 1	5 6
Control	none				
Coating Weight			222	297	255
Crystal Size			2 - 4	2 - 7	2 - 14
Coverage Rating			1	1	1

Coating weight - milligrams/Ft^2
Crystal size - microns

Table 12 presents the characteristics of the phosphate coatings formed on the metal substrates according to the process of the invention utilizing the activating Baths 14, 15, 16, 17, 18 and 19. The results shown in Table 12 were obtained utilizing the baths which had been aged for 90 days. It is clear that the 90 day old FIXODINE® Z8 bath (Bath 14) does not provide an acceptable phosphate coating on the surface of cold rolled steel, electrogalvanized steel or aluminum alloy 6061. However, application of ultrasonic energy to the aged bath (Bath 15), when in contact with the metal substrate produces excellent phosphate coatings on cold rolled steel, electrogalvanized steel and aluminum treated by the process of the invention.

Figures 23 (a), (b) and (c) are scanning electron photomicrographs at 1,000 magnification of panels phosphated utilizing the process of the invention and utilizing Bath 14 as the activating bath. Figure 24 is a scanning electron photomicrograph at 1,000 magnification of the crystal structure of the phosphate coating formed by the process of the invention on various metal substrates when ultrasonic energy is applied to Bath 15 while Bath 15 is in contact with the metal substrate. Figure 24 (a), (b) and (c) shows that cold rolled steel, electrogalvanized steel and aluminum alloy 6061 are provided with excellent phosphate coatings by the process of the invention.

Figure 25 is a scanning electron photomicrograph at 1,000 magnification of the phosphate coating provided on panels which were contacted with activating bath 15 five minutes after application of ultrasonic energy to the activating bath was discontinued. Figure 25 shows that the phosphate coating is acceptable even when the metal substrate is contacted with activating Bath 15 five minutes after the application of ultrasonic energy to the bath has been stopped.

Baths 14 and 15 produced coatings identical to the control bath after aging for one day. After aging for 90 days, the difference in the phosphate coating produced by the process due to application of ultrasonic energy to the activating bath can be clearly seen. Figures 23 through 25 show the effects of application of ultrasonic energy to the activating bath on the phosphate coating produced by the process of the invention. The coatings formed after the ultrasonic energy application had been discontinued 5 minutes before the panels were entered in the solution were satisfactory (see Figure 25).

Baths 16 and 17 contained a concentration of the activating composition only 1/3 of the concentration in Baths 11 and 12. Baths 16 and 17 showed a reduced activating ability after aging only one day. Bath 16, with stirring only, and contacted with the metal panel, produced a coating with larger crystal size and higher coating weights than Bath 14.

Figures 26, 27 and 28 show the coatings formed after aging the baths for 90 days. Panels treated with activating Bath 16 produced poor coatings when phosphated; however Bath 17 produced excellent phosphate coatings on cold rolled steel, electrogalvanized steel and aluminum alloy 6061 when ultrasonic energy was applied to the Bath 17 while activating Bath 17 was in contact with the metal substrate or within 5 minutes of stopping the application of the ultrasonic energy to the bath.

Phosphate coatings produced on cold rolled steel, aluminum alloy 6061 and electrogalvanized steel by the process using activating Bath 17 with application of ultrasonic energy to the activating bath when in contact with the metal panel were identical with phosphate coatings prepared by the process utilizing the control bath (Figure 32). The aluminum panel appeared to have several small voids in the coating where the metal surface could be seen in the scanning electron photomicrograph. After the application of ultrasonic energy to activating Bath 17 had been discontinued for 5 minutes, a slight loss of activating ability can be noted. The phosphated coatings produced by the process using activating Bath 17 with application of ultrasonic energy to the bath when in contact with the metal substrate were comparable to coatings produced from the fresh control bath containing 3 times the concentration of the FIXODINE® Z8 activating composition.

The PARCOLENE® Z bath which does not contain condensed phosphates, (Bath 18), produces poor coatings when the activating bath is prepared with tap water containing calcium and magnesium ion. After aging for only one day, the bath produced coatings similar to panels processed without contact with an aqueous activating bath. Activating Bath 19, to which ultrasonic energy was applied while in contact with the metal substrate, when phosphated, provided a coating comparable to the FIXODINE® Z8 Bath 14 on cold rolled steel and electrogalvanized steel. The coating produced by using activating Bath 19 on aluminum in the process was slightly more porous than that produced by using Bath 14. After the ultrasonic energy application had been discontinued for 5 minutes, the coatings on cold rolled steel and aluminum were similar to coatings produced by activating Bath 18, while the coating on electrogalvanized steel was excellent. Figures 23 through 31 and Figure 32 (control bath) illustrate the improved coatings provided by the process of the invention.

The experiments and the figures clearly illustrate that application of ultrasonic energy to an aqueous activating bath in a phosphate coating process improves the coating weight and crystal morphology of the phosphate coating. The application of ultrasonic energy to the activating bath extends the useful life of the bath. Extension of the useful life of the activating bath provides a process in which the activating bath is discarded at more extended intervals and therefore reduces the effect of the process on the environment.

The examples and the figures clearly show that phosphate coatings can be improved by the process of the present invention if ultrasonic energy is applied to the aqueous activating composition (activating bath) when not in contact with a metal substrate or when the aqueous activating bath is in contact with the metal substrate which is subsequently to be coated with a phosphate conversion coating.

The process of the present invention with the improvement of applying ultrasonic energy to the aqueous activating bath in the process, as shown by the examples and figures, improves the phosphate coating produced by the process and extends the life of the aqueous activating composition. Aged baths retain their activating ability over extended periods. In addition, the activating bath can contain lower concentrations of the activating composition and still be useful in activating the metal substrate in a phosphate coating processes. The lower concentrations of the activating composition, which can be used in the activating bath along with the longer useful life of the activating bath, provides a less expensive and more environmentally friendly process.

We claim

1. An improved process for forming a phosphate conversion coating on a metal substrate, wherein the surface of the metal substrate is cleaned, activated by contact with an aqueous activating composition and coated by a conversion coating process, the improvement which comprises: applying ultrasonic vibration energy to the aqueous activating composition.

2. The process of claim 1 wherein the ultrasonic vibration energy is applied to the aqueous activating composition in the presence of the metal substrate to be activated.

3. The process of claim 1 wherein the ultrasonic vibration energy is applied to the aqueous activating composition in the absence of the metal substrate.

4. The process of claim 1 wherein the surface of the metal substrate comprises a metal selected for the group consisting of iron, zinc, zinc alloys, aluminum and aluminum alloys.

5. A process of claim 1 wherein the aqueous activating composition contains water and an activating composition comprising titanium and phosphorous.

6. A process of claim 5 wherein the aqueous activating bath comprises a reaction product of a titanium compound and a phosphorous compound.

7. A process of claim 1 which comprises: (1) cleaning the surface of the metal substrate with an alkaline cleaning composition; (2) contacting the clean surface of the metal substrate with a titanium and phosphorous containing aqueous activating composition to which ultrasonic vibration energy is applied and (3) forming a phosphate conversion coating on the metal surface which has been contacted with the titanium and phosphate containing activating composition.

8. A process of claim 7 wherein the aqueous activating composition comprises from about 2 to about 30 parts per million of titanium.

9. A process of claim 1 wherein the aqueous activating composition comprises from about 2 to about 30 parts per million of titanium.

10. A process of claim 1 wherein the aqueous activating composition contains water, a reaction product of a titanium compound with a phosphorus compound, and a condensed phosphate.

11. A process of claim 5 wherein titanium and phosphorus are provided by a composition comprising the reaction product of a titanium compound with a phosphate compound.

12. A process of claim 11 wherein the metal substrate is contacted with the aqueous activating composition at a temperature of from ambient to about 150°F.

13. A process of claim 3 wherein the metal substrate is contacted with the aqueous activating composition in an activating zone and the ultrasonic vibration energy is applied to the aqueous activating composition in an ultrasonic zone outside of the activating zone.

14. A process of claim 1 wherein an average age of the aqueous activating composition is greater than five days.

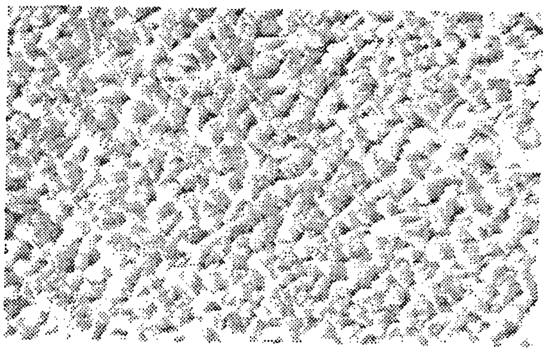


FIG. 1a

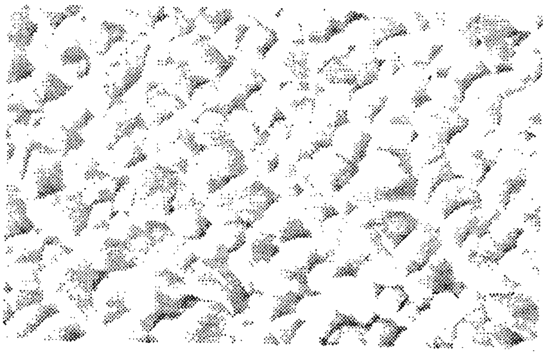


FIG. 1b

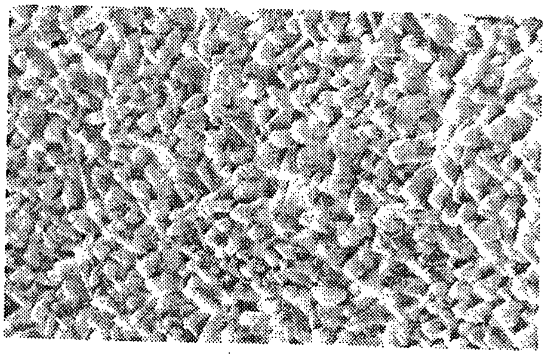


FIG. 1c

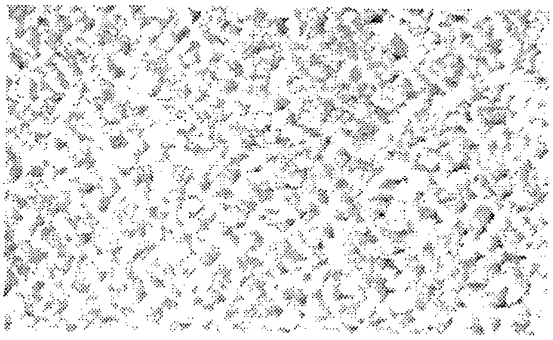


FIG. 2a

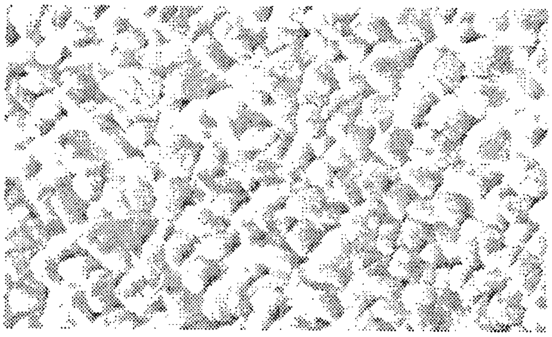


FIG. 2b

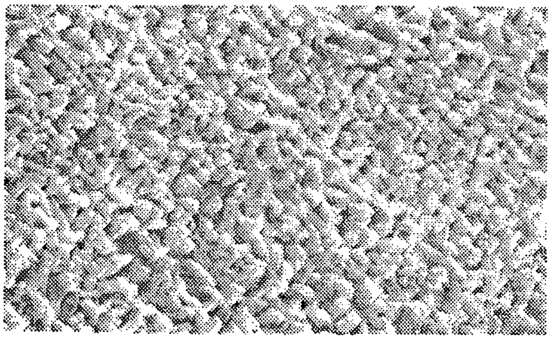


FIG. 2c

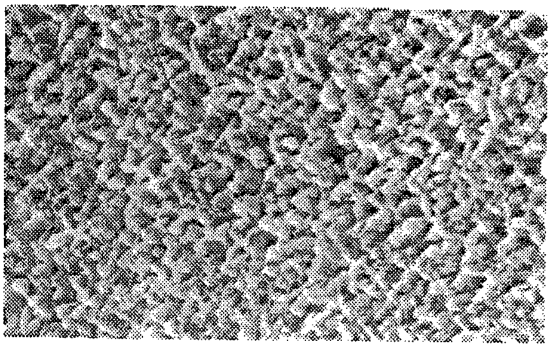


FIG. 3a

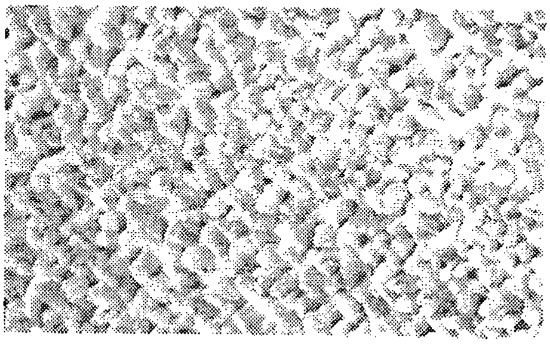


FIG. 3b

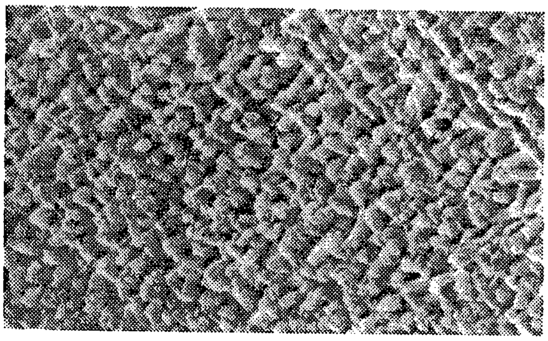


FIG. 3c

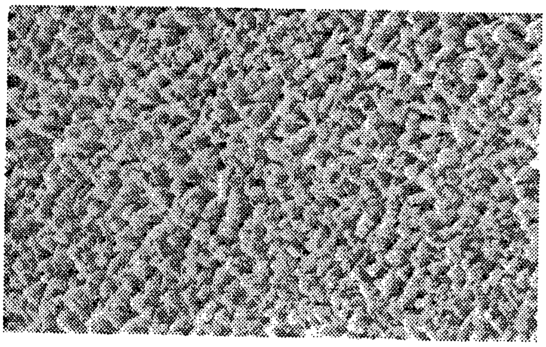


FIG. 4a

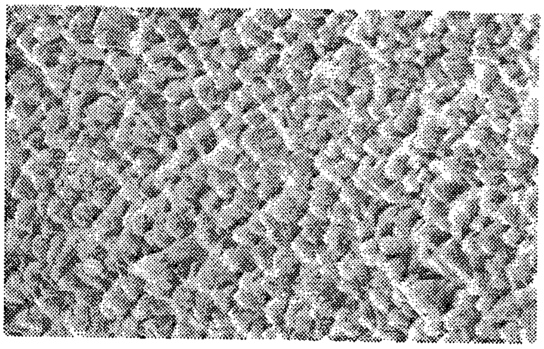


FIG. 4b

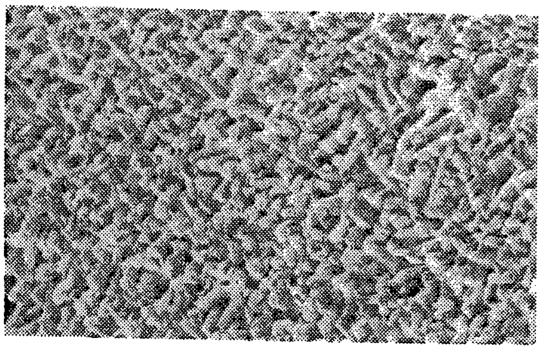


FIG. 4c

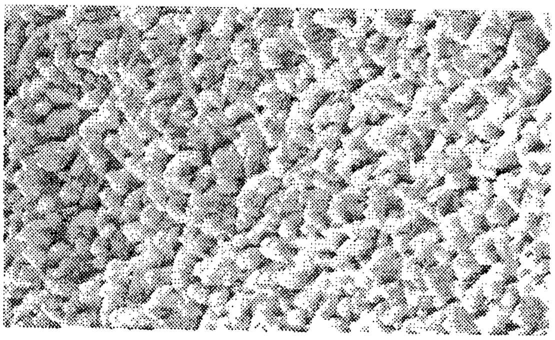


FIG. 5a

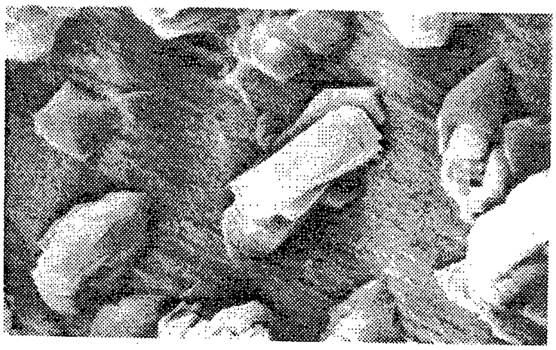


FIG. 5b

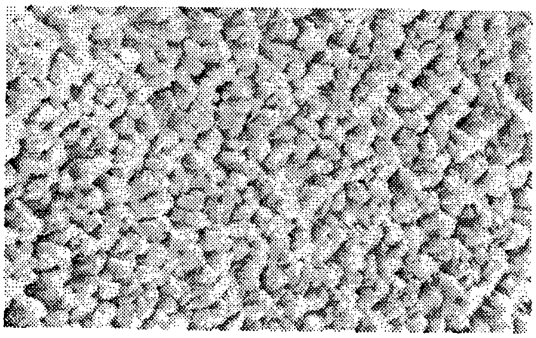


FIG. 6a

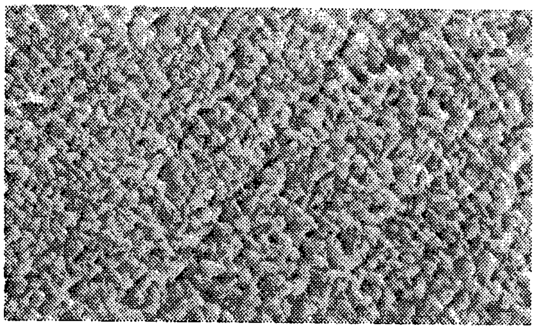


FIG. 6b

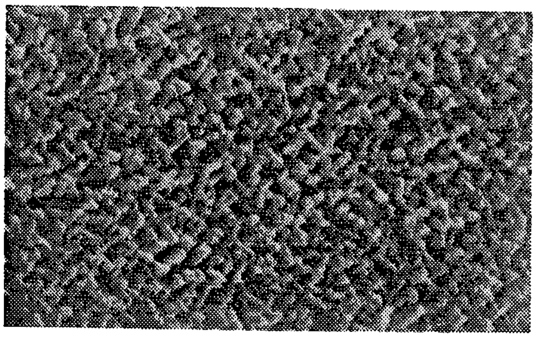


FIG. 6c

FIG. 7a

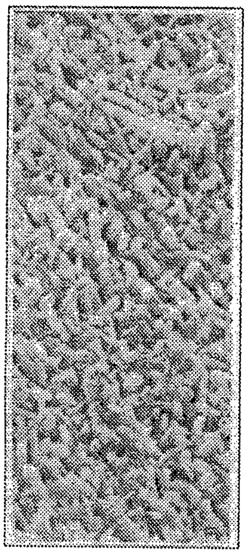


FIG. 7b

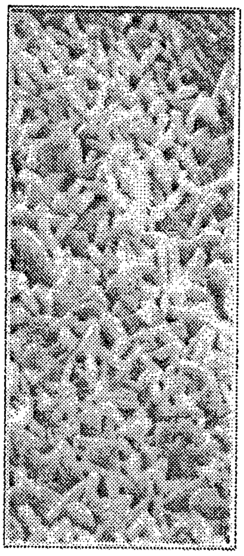


FIG. 7c

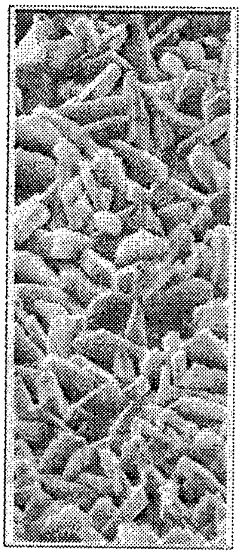


FIG. 7d

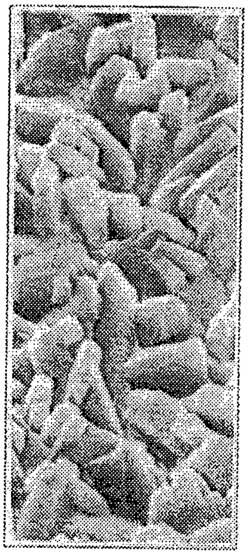


FIG. 8a

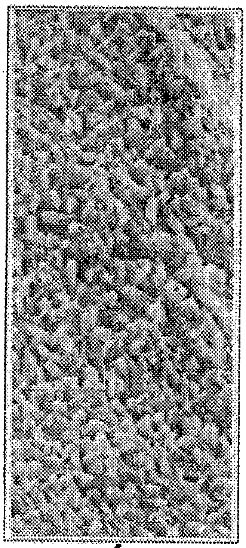


FIG. 8b

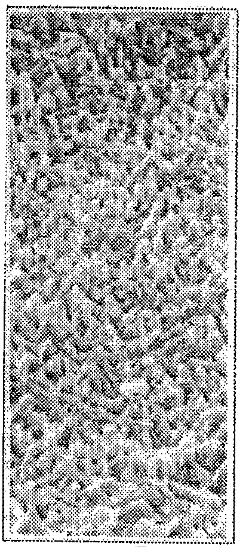


FIG. 8c

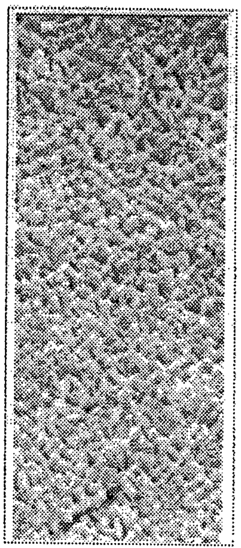


FIG. 8d

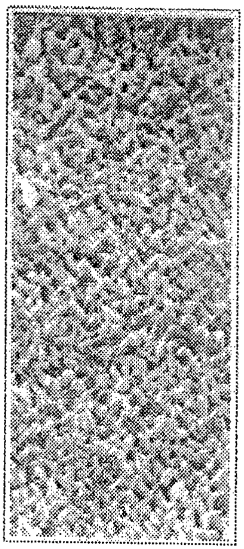


FIG. 9a

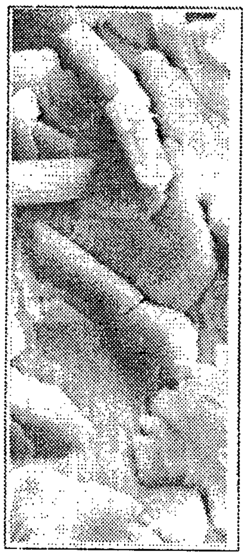


FIG. 9b

FIG. 9c

FIG. 9d

FIG. 10a

FIG. 10b

FIG. 10c

FIG. 10d

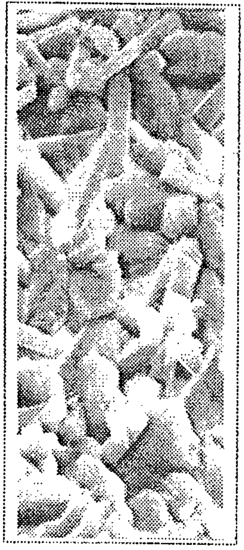


FIG. 11a

FIG. 11b

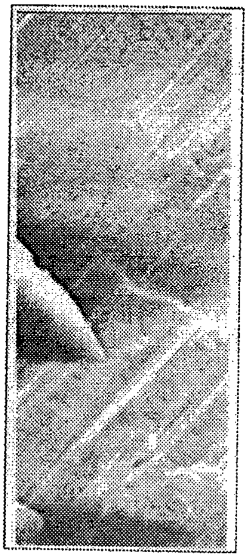


FIG. 11c

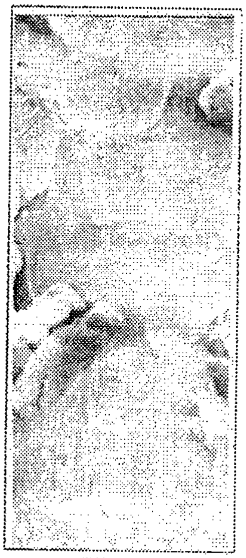


FIG. 11d

FIG. 12a

FIG. 12b

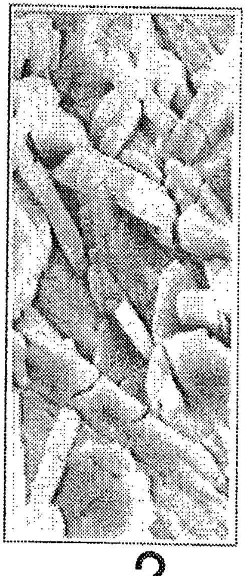


FIG. 12c

FIG. 12d

FIG. 13a

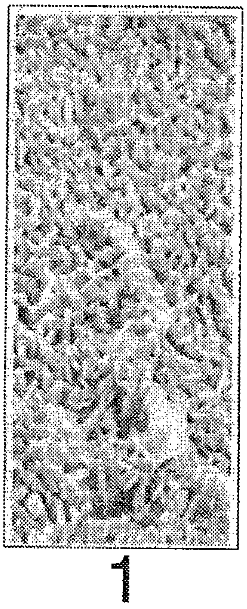


FIG. 13b

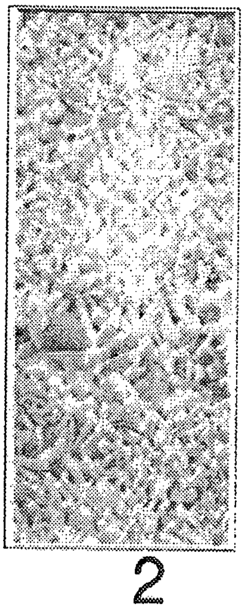


FIG. 13c

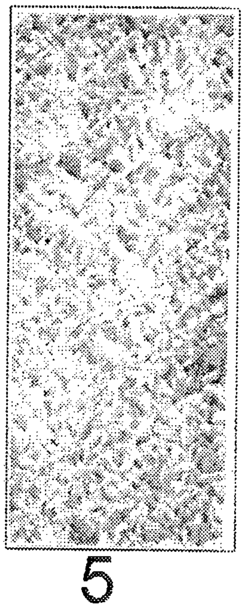


FIG. 13d

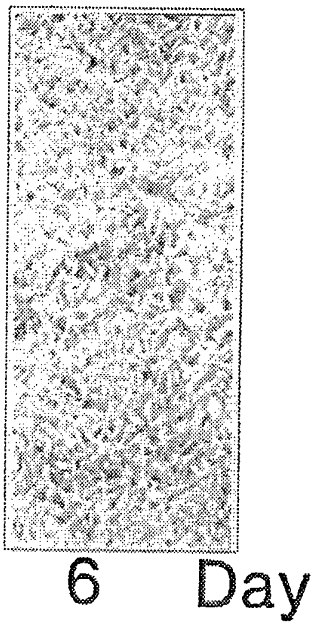
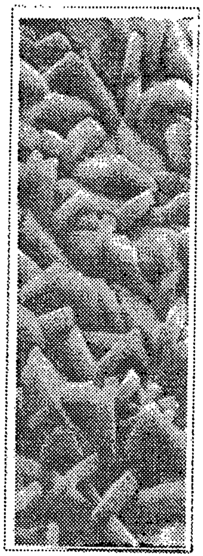


FIG. 14

FIG. 15a

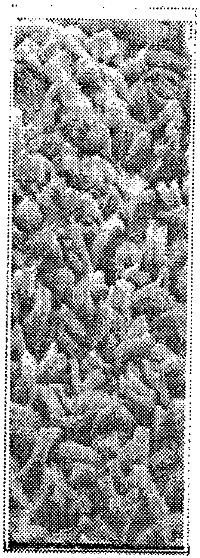


CRS
Sonicated

FIG. 15b

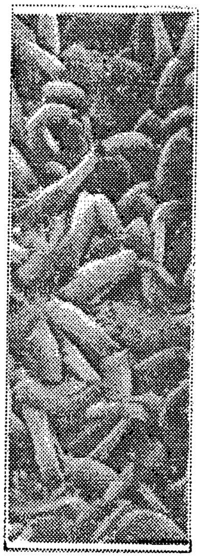
EG
Stirred

FIG. 15c



EG
Sonicated

FIG. 15d

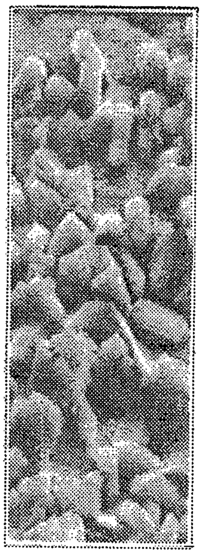


6061
Stirred

FIG. 15e

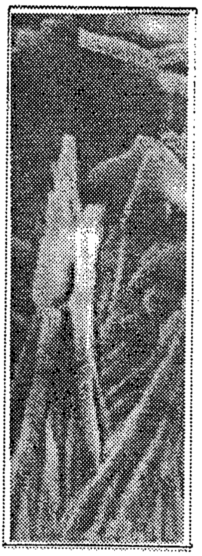
6061
Sonicated

FIG. 16a



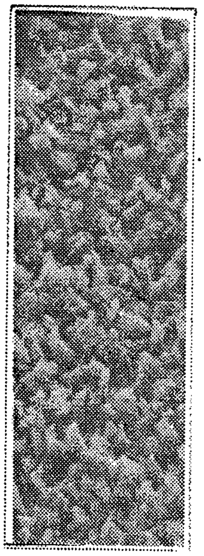
CRS
Sonicated

FIG. 16b



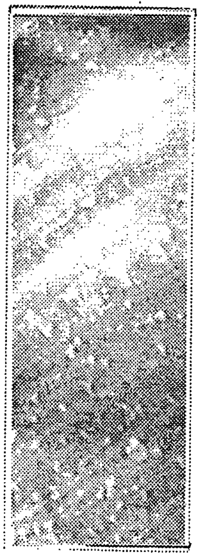
EG
Stirred

FIG. 16c



EG
Sonicated

FIG. 16d

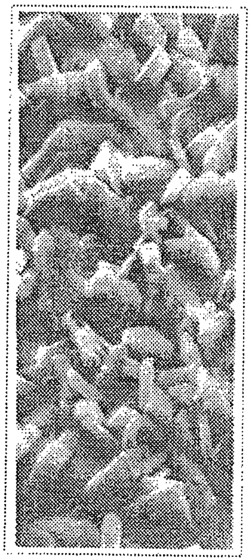


6061
Stirred

FIG. 16e

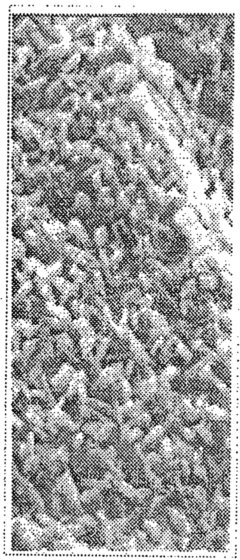
6061
Sonicated

FIG. 17a



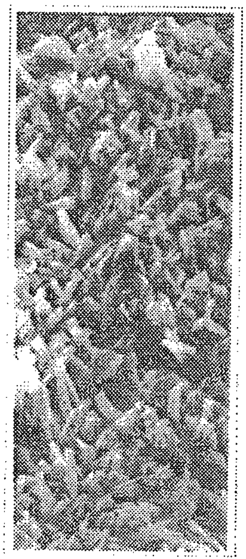
CRS
Stirred

FIG. 17b



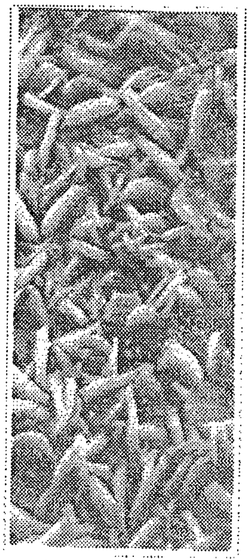
CRS
Sonicated

FIG. 17c



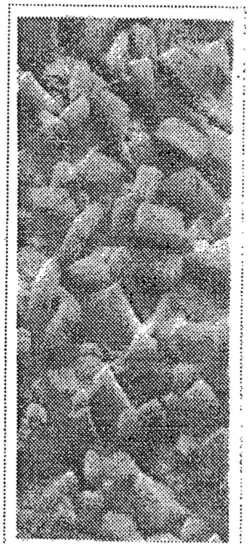
EG
Sonicated

FIG. 17d



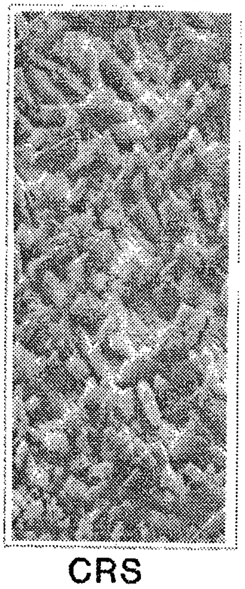
6061
Sonicated

FIG. 18a



CRS
Stirred

FIG. 18b

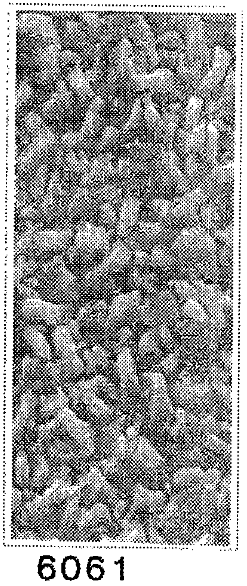


CRS
Sonicated

FIG. 18c

EG
Sonicated

FIG. 18d

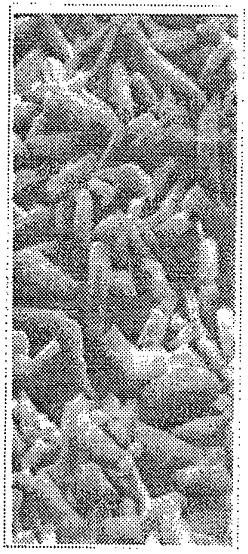


6061
Sonicated

FIG. 19a

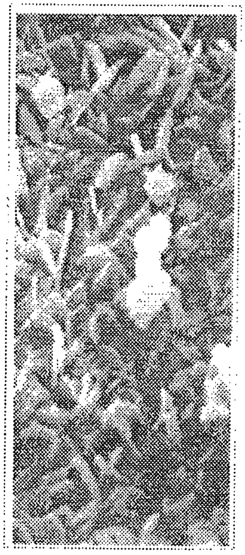
CRS
Stirred

FIG. 19b



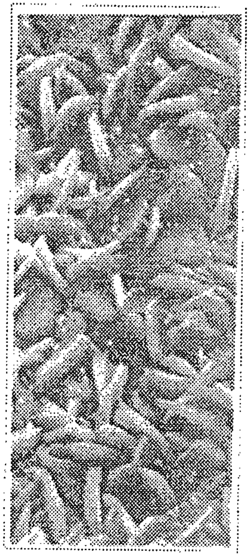
CRS
Sonicated

FIG. 19c



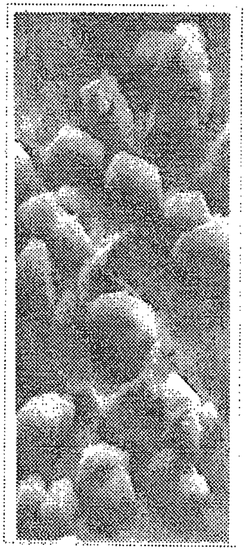
EG
Sonicated

FIG. 19d



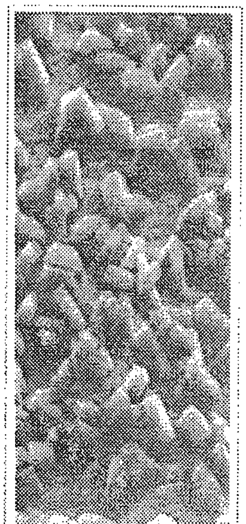
6061
Sonicated

FIG. 20a



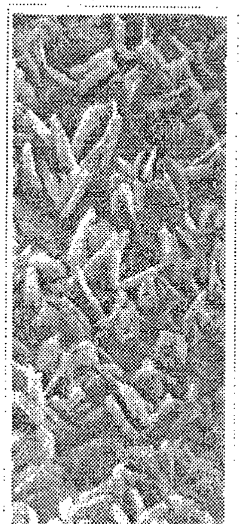
CRS
Stirred

FIG. 20b



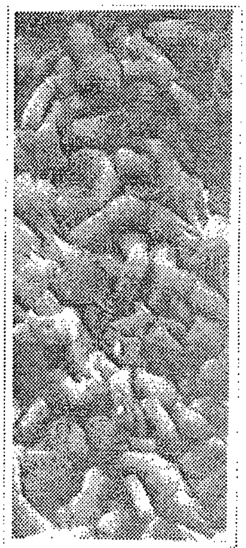
CRS
Sonicated

FIG. 20c



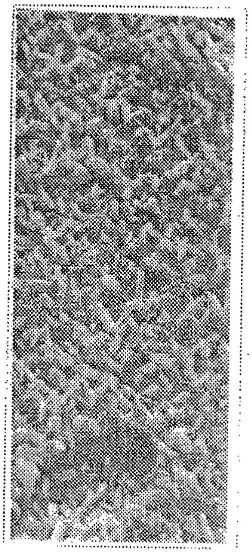
EG
Sonicated

FIG. 20d



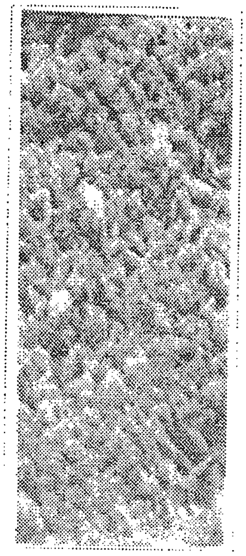
6061
Sonicated

FIG. 21a



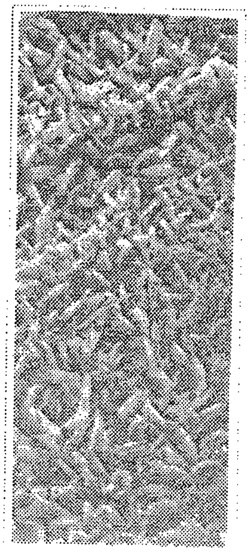
CRS
Stirred

FIG. 21b



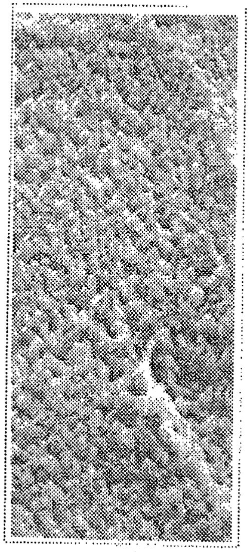
EG
Stirred

FIG. 21c



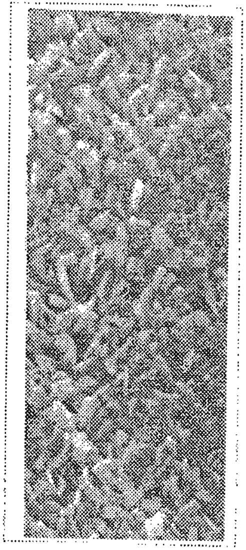
6061
Stirred

FIG. 22a



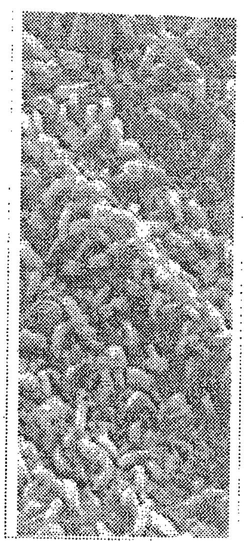
CRS
Stirred

FIG. 22b



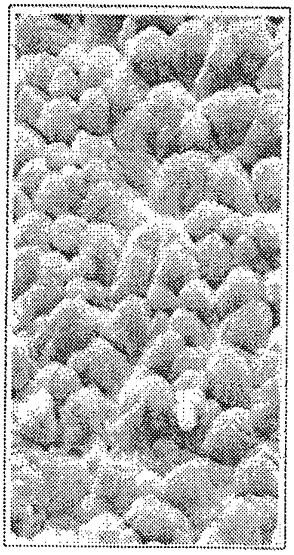
EG
Stirred

FIG. 22c



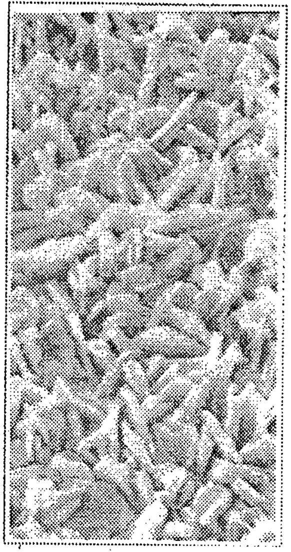
6061
Stirred

FIG. 23a



CRS

FIG. 23b

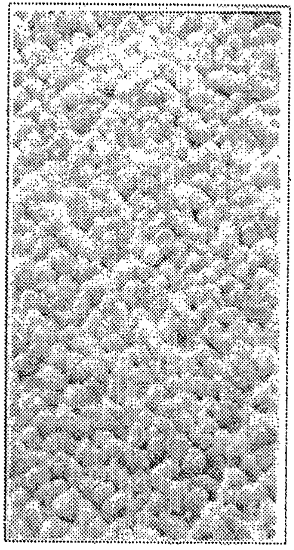


EG

FIG. 23c

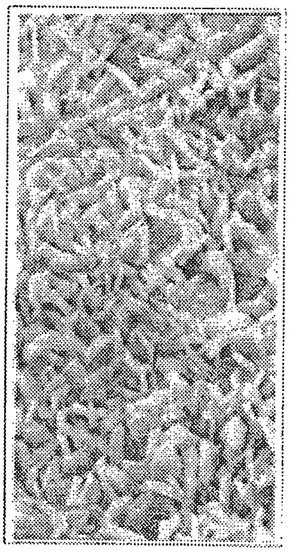
6061

FIG. 24a



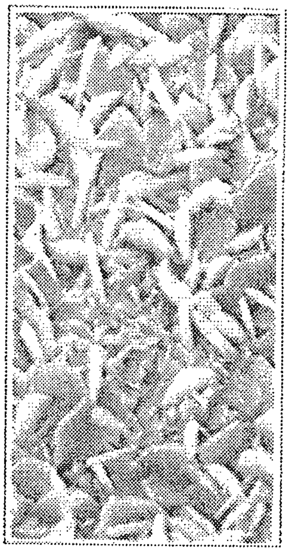
CRS

FIG. 24b



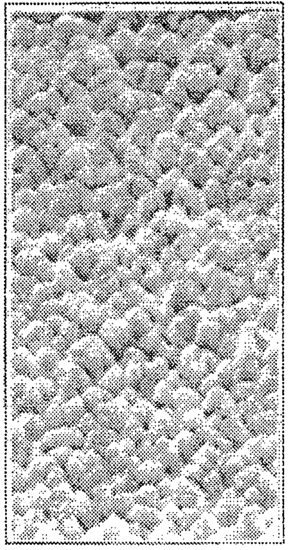
EG

FIG. 24c



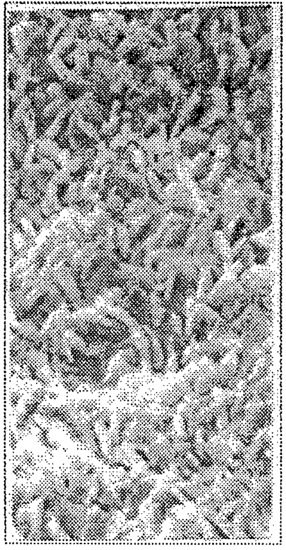
6061

FIG. 25a



CRS

FIG. 25b



EG

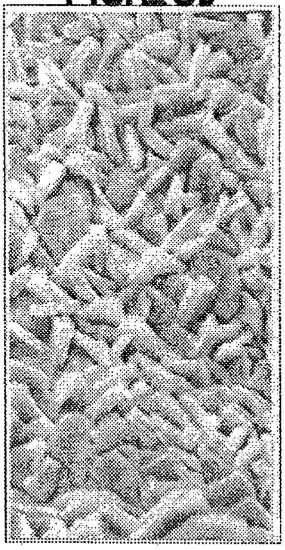
FIG. 25c

6061

FIG. 26a

CRS

FIG. 26b

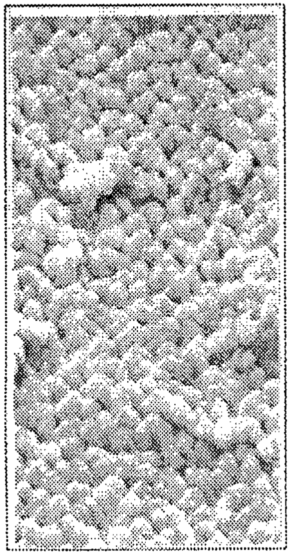


EG

FIG. 26c

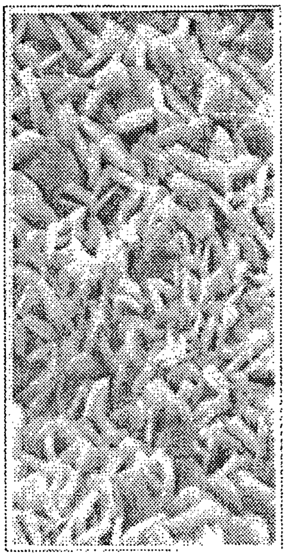
6061

FIG. 27a



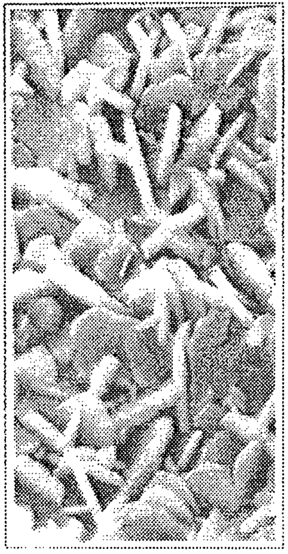
CRS

FIG. 27b



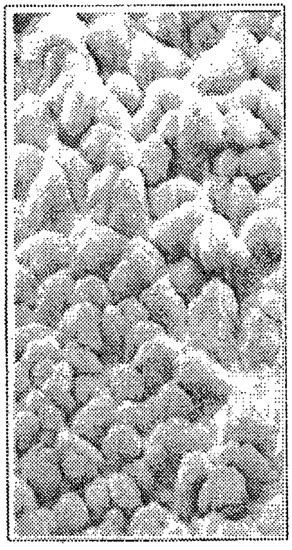
EG

FIG. 27c



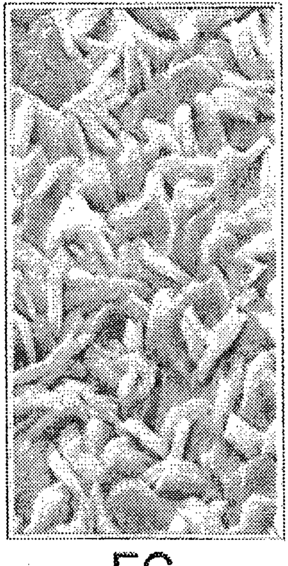
6061

FIG. 28a



CRS

FIG. 28b



EG

FIG. 28c

6061

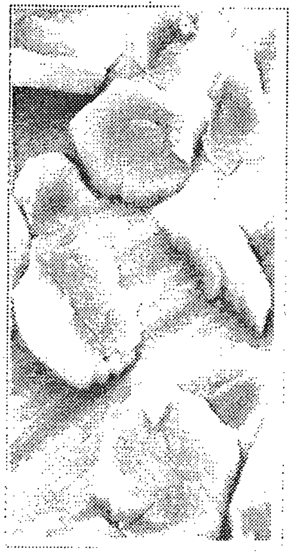
FIG. 29a

CRS

FIG. 29b

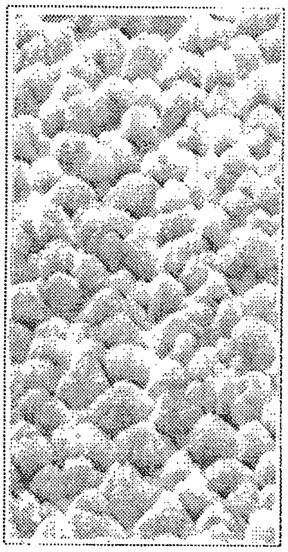
EG

FIG. 29c



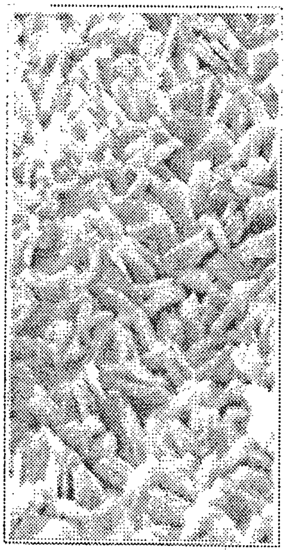
6061

FIG. 30a



CRS

FIG. 30b



EG

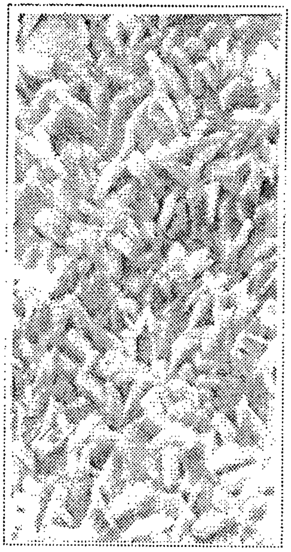
FIG. 30c

6061

FIG. 31a

CRS

FIG. 31b

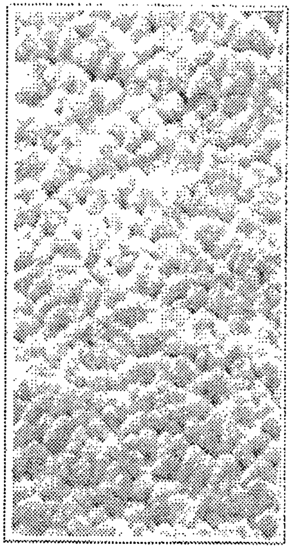


EG

FIG. 31c

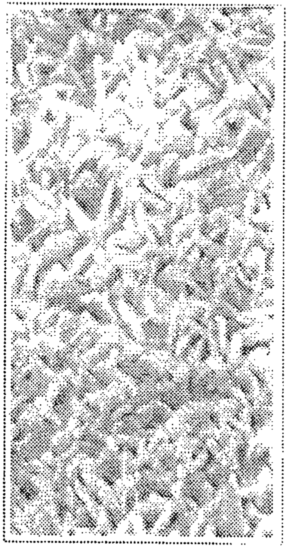
6061

FIG. 32a



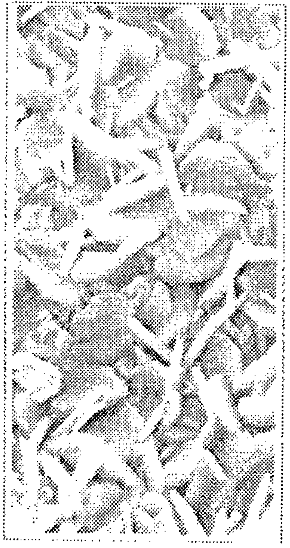
CRS

FIG. 32b



EG

FIG. 32c



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10243

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C23C 22/80
US CL :148/241, 254
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/241, 254

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP,A, 61 170576 (KAWASAKI STEEL) 01 August 1986 see abstract	1-14
Y	US,A, 2,456,947 (Jerustedt) 12 December 1948. See col. 2 lines 40-68	1-14
Y	US,A, 4,531,978 (Otrhalek et al) 30 July 1985 see col. 3	1-14
Y	US,A, 4,529,451 (Otrhalek et al) 16 July 1985 Col. 1 lines 60-68.	1-14

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search

11 JANUARY 1994

Date of mailing of the international search report

23 FEB 1994

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