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CALORIZING PROCESS

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The present invention relates to the process of calorizing metal surfaces. Calorizing is the term used to describe the formation of a surface alloy composed of aluminum and the metal being calorized. Such an alloy of aluminum and the base ferrous and non-ferrous metal protect the base metal against the deleterious effects of heat and/or oxygen. The alloy formed by the calorizing process is rich in aluminum at the surface and decreases in aluminum content as the depth of the alloy increases. On exposure to the atmosphere the aluminum skin immediately oxidizes to form a protective layer of aluminum oxide which is self-healing if mechanically broken as long as any aluminum is present in the alloy layer.

The fact that ferrous or copper surfaces could be provided with a protective surface alloy of aluminum and the foundation metal has been known for over thirty years and various processes have been developed for obtaining the desired result. One early process included heating the article to be treated in contact with aluminum powder and a flux in a non-oxidizing atmosphere. Another comprises dipping the article in molten aluminum and firing the coated product. As both of these processes are rather wasteful and expensive as to the amount of aluminum required for the treatment, attempts have been made to apply the aluminum in the form of a suspension of aluminum powder in a suitable medium. For example Patent 1,655,269, Howe recommends coating the foundation metal with aluminum powder in combination with a cellulose binder.

While this painting or coating method has been known for about twenty years and was originally considered as having certain advantages, i. e., decreased cost and wider application to articles of large sizes which should have made it an acceptable substitute for the earlier known processes, the fact is that its commercial use has been comparatively limited. It has been found that with the paints or coating compositions employed heretofore results were not consistently reproducible and there were frequent cases of failure due to incomplete coverage or alloying. This was particularly noted on parts having irregular surface contours such as threaded portions and the like. It now appears that this limited commercial success of the paint method was to a large extent due to the form of the finely-divided aluminum employed. The net result was that the foundation metal was not in sufficiently intimate contact with aluminum during firing to obtain a uniform and effective calorization of all types of surfaces.

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The present invention is based on the discovery that the paint or coating process can be applied successfully in the calorizing of articles of all types and shapes by employing, as the coating material, a suspension of both flake and granular aluminum in specific proportions. More particularly, it has been found that the suspension should contain from 55 to 65 per cent by weight of finely divided aluminum capable of passing through a 100 mesh screen, the aluminum content consisting by weight of from 65 to 75 per cent, preferably about 70 per cent granular aluminum and from 25 to 35, preferably about 30 per cent, flake aluminum. Any suitable fugitive suspension medium can be employed.

The unexpected advantages resulting from the use of both granular and flake aluminum in the specified proportions have been demonstrated by numerous tests on different types of surfaces using coating compositions containing various proportions of flake and granular aluminum. The following series of tests are set forth as illustrating the advantages of the present invention as applied to test pieces having both flat and angular or irregular surface portions. At least 85 per cent of the finely divided aluminum used in these tests was fine enough to pass through a 325 mesh screen. The binder was a clear lacquer comprising a solution of about one part nitrocellulose (solid basis) and two parts of an oil-modified alkyd resin (solid basis) dissolved in about 52 parts by weight of a solvent mixture including xylol and butyl acetate. The particular alkyd resin was a phthalic anhydride-glycerol-castor oil reaction product containing about 45 per cent castor oil. The various suspensions of finely-divided aluminum in the lacquer were adjusted by the addition of solvents to a density of 1.344 gm./cc. as it has been found that the quantity and consistency of the suspension should be held to the minimum required to suspend the aluminum. Preferably, the density of the aluminum-containing composition should be from 1.250 gm./cc. to 1.44 gm./cc. Specifically, in the following tests 287 cc. of the suspension medium was employed, the medium containing approximately 4.6 grams of nitrocellulose and 9.3 grams of the castor oil-modified alkyd resin on the solids basis.

Seven suspensions of finely divided aluminum in the above described lacquer were made up and numbered 1 through 7. Each of these compositions had the approximate volume of 500 cc. and are respectively identified in Table 1 by the numerals 1 to 7. Five of the suspensions, numbers

1 to 5 contained aluminum flake and aluminum powder in varying proportions while the other two contained either aluminum flake or aluminum powder.

Three sets of test pieces were used and each piece was numbered according to the coating applied thereto. One set was employed to determine the coverage power of the various suspensions and the other two were employed to determine the relative oxidation resistance of the coated parts.

The coverage test samples (Samples D, 1 through 7) were prepared from one-half inch diameter oxygen-free round copper stock. Each of the seven pieces were serrated with a series of seven annular grooves one-sixteenth inch wide, one-sixteenth inch apart, and starting one-sixteenth inch from one end of the bar. The first two grooves were .234 inch deep, the second two .218 inch deep, the third two .187 inch deep, and the final two .0625 inch deep.

Accelerated oxidation samples, (B, 1 through 7), were prepared from five-eighth inch hexagonal oxygen-free copper bar stock.

Accelerated oxidation samples, (C, 1 through 6), were prepared from one-half inch square oxygen-free copper bar stock. All samples were finally cut to a length of two inches.

The numbered sample bars were dipped into the various coating compositions of corresponding number and were suspended vertically to dry. Each of the suspensions was well agitated prior to and during dipping. After all of the samples had been dipped and thoroughly dried, they were fired in a reducing atmosphere at a temperature of 950° C. This temperature was sufficient to volatilize the resin binder and form the desired alloy surface. After firing, the sample bars were very lightly wire brushed to remove scale and tested for coverage and oxidation resistance.

As a coverage test, the grooved bars were sectioned on a milling machine; the cut removing exactly half of the diameter of the bar and extending along its major axis for one and one-fourth inches so that a cross section of the annular grooves resulted, this section was polished. The number of square surfaces (6 per groove) exposed on the plane of the cut were totaled. For evaluation number 1, the number of these surfaces, the sides and root of the cuts, or edges which showed an unbroken calorized layer were counted. The percentage of such calorized surfaces based upon the total number of surfaces exposed was recorded as the per cent coverage, Evaluation #1. These sectioned bars were then placed in an ordinary air atmosphere at a temperature of 950° C. for one-half hour. The exposed copper was oxidized to the characteristic blue-black color which sharply defined the bright yellow calorized layer. The surfaces (sides and bottoms of the grooves) which showed an unbroken calorized layer were again counted and the per cent coverage again calculated and recorded as coverage, Evaluation #2.

For an accelerated oxidation test, the two sets of sample bars, B and C, were weighed and placed in a furnace at room temperature, total exposure time at temperatures from 600° C. to 950° C. sixty-four hours. These sample bars after cooling, were re-weighed. The per cent weight gain was calculated. The average weight gain of the corresponding samples of the two sets was calculated and recorded as average per cent weight gain due to oxide. These results are also shown in Table #1.

Jar	Aluminum Flake		Aluminum Powder		Sample D, Per Cent Coverage Evaluation		Samples B & C Oxidation Weight Gain, Avg. Per Cent
	Per Cent	Gms.	Per Cent	Gms.	#1	#2	
1	10	44	90	393	89	77	.425
2	30	131	70	306	100	98	.13
3	50	218.5	50	218.5	85	80	.20
4	70	306	30	131	71	64	.245
5	90	393	10	44	60	48	.39
6	100	437			62	44	.38
7			100	437	64	67	.46

From the results of the above tests and from experience in the commercial practice of the present invention it has become apparent that while suspensions of granular aluminum powder give about 15 per cent better coverage than similar suspensions of aluminum flake, a mixture of about 30 per cent aluminum flake, and 70 per cent aluminum powder is superior to both. These conclusions are also supported by the oxidation tests run on Samples B and C in that the average weight gain for the samples coated only with powder or only with flake aluminum show an average weight gain of about three times that of samples coated with the mixture of flake and powder within the scope of the present invention.

While the invention has been specifically described with reference to the use of a binder comprising a mixture of nitrocellulose and a particular oil-modified alkyd resin in specific proportions, it is to be understood that it is not limited thereto. Experience has shown that the aluminum composition is the more important factor in this invention and that any resinous or non-resinous liquid carrier medium which will suspend the aluminum and will volatilize before or during the firing process will produce acceptable results. For example, suspension mediums consisting of toluol fortified with stearic acid as a lubricant or mineral spirits alone have given good results. A suitable suspension medium may be broadly defined as one which is entirely removed from the surface of the coated article either by decomposition or evaporation or both at a temperature below 600° C., the temperature at which or above which the aluminum alloys well with the base metal to form the desired calorized surface.

When an alkyd-modified pyroxylin binder is used, it may comprise anywhere from about one to three parts of the alkyd resin for each part nitrocellulose, and cocoanut oil, linseed oil, soya bean oil may be substituted for the castor oil content of the oil-modified alkyd. The non-drying or semi-drying oils are ordinarily preferred. The selection of the binder emphasized here is prompted by the toughness it imparts to the aluminum coat which materially reduces probability of damage to the coating by handling prior to firing. It is also to be understood that unmodified pyroxylin lacquers can be used as binders and suspension mediums for the mixtures of aluminum flake and aluminum powder.

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

1. The process of protecting metal articles from oxidation which comprises applying to the surface of the article a coating of a composition comprising a suspension of finely-divided aluminum in a fugitive liquid carrier medium comprising a resin which will decompose and evaporate at a temperature below 600° C., the aluminum

comprising a major portion by weight of said composition, and firing the coated article at a temperature of at least 600° C. to drive off the suspension medium and alloy the aluminum with the surface metal of the article, said finely-divided aluminum consisting of from 65 to 75 per cent granular aluminum powder and from 25 to 35 per cent flake aluminum.

2. The process of protecting metal articles from oxidation which comprises applying to the surface of the article a coating of a composition comprising a suspension of a major portion of finely-divided aluminum in a minor portion of a liquid suspension medium which will decompose and evaporate at a temperature below 600° C., and firing the coated article at a temperature of at least 600° C. to drive off the suspension medium and alloy the aluminum with the surface metal of the article, said finely-divided aluminum consisting of from 65 to 75 per cent granular aluminum powder and from 25 to 35 per cent flake aluminum.

3. The process of calorizing the surface of a metal article which comprises coating the desired surface areas of said article with a composition comprising from 55 to 65% by weight of finely-divided aluminum suspended in a liquid carrier medium containing nitrocellulose, drying the coating and firing the coated article at a temperature sufficient to decompose the binder and alloy the aluminum with the surface metal of the article, said finely-divided aluminum consisting of 65 to 75 per cent granular aluminum powder and 25 to 35 per cent flake aluminum at least 85 per cent of which will pass through a 100 mesh screen.

4. The method of calorizing the surface of a metal article which comprises coating the desired surface area of the article with a composition comprising from 55 to 65% by weight of a suspension of finely-divided aluminum in a binder and suspending medium comprising a solution of about one part nitrocellulose and from one to three parts of an oil-modified alkyd resin in an organic solvent, drying the coating and firing the coated article to decompose the binder and alloy the aluminum with the surface of the metal article, at least 85 per cent of said finely-divided aluminum passing through a 100 mesh screen area consisting of from 65 to 75 per cent by weight of granular aluminum powder and 25 to 35 per cent by weight of flake aluminum.

5. The method of claim 4 wherein the alkyd resin is a castor oil-modified phthalic anhydride, polyhydric alcohol resin reaction product containing about 45 per cent castor oil.

6. The method of claim 2 wherein the suspension medium is a volatilizable organic liquid.

7. The method of claim 2 wherein the suspension medium is a fluid mixture of toluol and stearic acid.

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