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BATH FOR THE ANODIC OXYDATION OF ALUMINIUM AND ITS ALLOYS FOR OBTAINING VERY HARD AND TOUGH FILMS

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It is known that in the electro-chemical processes of anodic deposition and oxydation it is of outstanding importance to employ organic substances and colloids, which provide improved eveness in the deposition and film formation, and determine special characteristics in said films. In the specific case of oxydation of aluminium the obtention of a very hard film of oxyde, resisting to the action of chemical agents is desired.

The aluminium oxyde which would most satisfactorily correspond to those physical-chemical characteristics is the crystalline oxyde called corundum, having a hardness corresponding to 9 in Mohs' scale. The process according to the invention has the object of obtaining particularly hard and wear-proof films on pure aluminium and its usual alloys, so that such hardness, which can be measured by a diamond sclerometer, be the highest obtainable, the oxyde film possessing, however, all the characteristics which might be required by the different uses of said objects.

For sake of accuracy, the films may be subdivided into the following types:

Type 1.—A very hard film, with limited flexibility, suitable for prevent blocking of fittings, bolts, and any other threaded pieces made of aluminium and its alloys, which film may possess a considerable porosity which allows to color the same by absorption of coloring solutions, for colored objects to be subjected to wearing or rubbing.

Type 2.—A soft, but very porous and flexible film, such as to allow molding of already oxydised pieces or forming a white or colored pigment in the same film to give lacquered-like appearance to the objects, while retaining, however, the characteristics of the anodic film.

Taking the well known aqueous solution of sulphuric acid as the main electrolyte, additions of organic substances have been tested and, through numerous tests, the decisive influence of polyhydric alcohols and chiefly of those methyl-cellulose complexes which are known by the tradename of Tylose has been ascertained; with the presence of the latter complexes, the presence of the above polyhydric alcohols may be dispensed with.

Another product having also a considerable influence on the hardening of the films in question is the so-called Gulac, which is a sub-product of the sulphite cellulose manufacture, cited e. g. in the "Journal of Research of the National Bureau of Standards" of the U. S. Dept. of Commerce, Vol 13, Sept. 1934, No. 3, page 335.

Several examples are described hereinafter, which correspond to the above listed types of films.

EXAMPLE I (TYPE 1).—*For very hard, color-absorptive films, with limited flexibility*

15 Kg. of sulphuric acid at 66° Bé. are added to 85 litres of distilled water and, after cooling, 100 g. of Tylose or methylcellulose, are also added.

The bath thus composed has an optimum operation between 15° C and 21° C, giving, however, quite satisfactory films even at 13° C, with a potential from 9 to 15 Volt, the optimum being 12,5 Volt and with a density of current of about 0,8 Ampère per sq. dm. for pure aluminium and rolled or drawn alloys and with a density of current of 1–2 Ampère per sq. dm. for cast alloys. The film is colorless and transparent, vitreous and very hard and yet susceptible of being colored by dipping or other methods with direct coloring agents, or by reaction.

The duration of the oxydizing treatment may be from 20' to 1 hour and can give films up to 0,06 mm thick. The hardness is surprising and the values for the different alloys in grams of load on the diamond point required to scratch the oxyde film down to the underlying metal are the following:

	Film obtained by the present process	Maximum of other processes
	Grams	*Grams*
Cast anticorodal	246	210
Drawn anticorodal bar	227	186
Semi-raw aluminium sheet	184	150
Rolled avional	137	100
Rolled Duraluminium	111	85

It is evident that the results are most satisfactory and afford the advantage of allowing to color films of even exceptional hardness, which heretofore had to be left with their natural color.

EXAMPLE II (TYPE 1.)—*For very hard films, with comparatively limited porosity*

15 Kg. of sulphuric acid at 66° Bé. are added to 85 litres of distilled water and, after cooling, 2–3 Kg. of a polyhydric alcohol, preferably glucose, and 0,5 Kg. of Gulac are added.

The bath thus composed provides optimum operation at temperatures from 15° C to 19° C, quite satisfactory films being obtained, however, even at 13° C, with a potential from 10 to 15 volts and a density of current of about 0,8 ampère per sq. dm. for pure aluminium and rolled and drawn

alloys, and a density of current of ½ ampère per sq. dm. for cast alloys. The film is colorless, transparent and vitreous and gets still harder after immersion in water at 80–85° C for 10–20 minutes. The duration of the oxydizing treatment may be from 20′ to 1 hour, giving a thickness up to 0,06. The hardness is exceedingly high and is listed in the following table, which includes the results obtained with different alloys and pure aluminium. The second column shows the maximum results obtained by the other processes used heretofore.

The values are given in grams of load on the diamond point required to scratch the oxyde film down to the underlying metal.

	Film obtained by the present process	Maximum of other processes
	Grams	*Grams*
Cast anticorodal	248	210
Drawn anticorodal bar	226	186
Semi-raw aluminium sheet	188	150
Rolled avional	136	100
Rolled Duraluminium	110	85

The influence of the addition of Gulac or polyhydric alcohols is evident; Gulac, however, has an outstanding influence on the result, as the mere addition of polyhydric alcohols, though it gives better results than other processes, does not reach the above figures which represent the average of many tests.

EXAMPLE III (TYPE 1).—*For hard porous layers to be coloured*

20–22 Kg. of sulphuric acid at 66° Bé are added to 80/78 litres of distilled water and, after cooling, 1–1,5 Kg. of a polyhydric alcohol, preferably glucose, and 1 Kg. of Gulac are added. The bath thus composed operates the best at a temperature between 17° and 23° C., giving most satisfactory films even at 16° C., with a potential from 12 to 15 volts and a density of current of 0,9 ampères per sq. dm. for pure aluminium and drawn and rolled alloys, and a density of current of 1-2 ampères per sq. dm. for cast alloys.

The film is colorless and transparent, very hard and capable of being colored by immersion or other system by direct coloring agent or by reaction. The hardness is still decisively higher than with similar coloring processes.

EXAMPLE IV (TYPE 1).—*For films for flexible objects or objects to be molded*

30 Kg. of sulphuric acid at 66° Bé are added to 70 litres of distilled water and, after cooling, 120–150 grams of methyl-cellulose or Tylose are added. Operation requires 12 volts and 0,8 ampères per sq. dm. for aluminium or rolled or drawn alloys, and 1-2 ampères per sq. dm. for cast alloys, between 18° and 23° C. according to whether absorption of a dyestuff or pigment is desired.

The hardness figures, considerably lower and slightly different for various alloys are still superior to those obtained by other processes; for aluminium, for instance, the load is still 100 grams with the present process, while it is only 80 grams with other processes.

EXAMPLE V (TYPE 2).—*For relatively scarcely hard but porous film for flexible objects or objects to be moulded*

30 Kg. of sulphuric acid at 66° Bé are added to 70 litres of distilled water and, after cooling, 3 kg. of a polyhydric alcohol and 2 kg. of Gulac are added.

Operation is carried out with 12 volts and 0,8 ampères per sq. dm. for rolled or drawn aluminium or alloys and with 1–2 ampères per sq. dm. for cast alloys, from 18° and 23° C. according to whether dyestuff or pigment is to be absorbed.

The hardness figures, considerably lower and slightly different for various alloys, are still superior to those obtained by other processes; for aluminium, for instance, the load is still 100 grams with the present process, while it is only 80 grams with other processes.

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