United States Patent Office 2,921,865
Patented Jan. 19, 1960

2,921,865

METHOD OF FORMING COLD EXTRUSION LUBRICANTS HAVING A ZINC PHOSPHATE UNDERCOATING

William L. Kubie, Riverside, Calif., assignor, by mesne assignments, to Aluminum Research Corporation, a corporation of Delaware

No Drawing. Application April 2, 1958
Serial No. 725,787

2 Claims. (Cl. 117—89)

This invention relates to the art of the cold extrusion of metal billets and particularly to a method of forming a cold extrusion lubricant having a zinc phosphate undercoating.

In the cold extrusion of metals such as aluminum and its alloys, a lubricant composition is applied to the die contacting surfaces of the billet to be extruded. A typical and commonly employed lubricant utilizes stearates with phosphate base. Such lubricant coating compositions have been described by John S. Thompson in Patent No. 2,234,206 and Patent No. 2,312,855.

Preparing a billet for phosphate lubricating includes three main steps: cleaning and conditioning of the surface of the billet; precipitating the phosphate coating; and reacting the lubricant with the phosphate undercoating. The present invention is directed to a process for controlling this third and final step.

The composition used for forming the lubricant film on the phosphate undercoat is a lubricating bath comprising a solution or suspension of zinc stearate, sodium stearate and buffers for pH control.

As used in this specification, the term stearates shall be understood to mean the commercial stearates which usually comprise mainly stearates and palmitates and include small percentages of higher and lower molecular weight fatty acids.

In order to provide an effective coating it is known that the free acid concentration of the bath must be maintained at a predetermined level. During the use of the lubricating bath the free acid tends to drop off. Conventionally, the free acid concentration is maintained by the addition of concentrated sulfuric acid. The reaction of the acid with the constituents of the bath adds to the total salt content of the bath and causes the salting out of soaps and fatty acids in solution and suspension. In addition, the salting out effect causes a repression of the free stearic acid and as a result, the reaction of the phosphate undercoat with the lubricating solution is often erratic in both time and amount. The resulting coating is often powdery and tends to flake off causing unsatisfactory extrusion and surface finishing and "stick-slip" in the extrusion itself.

Accordingly, it is an object of this invention to provide a method of forming the lubricant coating which overcomes the above disadvantages.

It is a further object of this invention to provide a method for maintaining the free acid content of the bath at a substantially high level and minimizing the salting out effect.

It is a further object of this invention to provide a method of applying a phosphate-type cold extrusion lubricant to a metal billet whereby an improved lubricating coating is formed.

It is a more particular object of this invention to provide a method for controlling the reaction in the lubricating bath of a phosphate coated metal article to form billets having a uniform lubricant coating.

Other objects and advantages of this invention will be

apparent, it is believed, from the following detailed description of a preferred embodiment thereof.

In preparing a billet for extrusion the surface of the billet is first cleaned by conventional methods. Zinc phosphate is then precipitated out onto the cleaned surface. The coated billet is then placed in a lubricating bath where the final lubricant film forms.

The phosphating bath is generally a solution of zinc salts, including zinc tetra-hydrate orthophosphate, $Zn(H_2PO_4)_2$, and phosphoric acid. The lubricating bath is an aqueous solution or suspension of equal parts of sodium stearate and sodium palmitate and a mixture of buffering agents such as sodium tetraborate and sodium carbonate. The reaction between the aluminum billet and the phosphating bath whereby zinc phosphate is precipitated out of the clean surface of the billet is not completely understood but it is known that a substantially uniform zinc phosphate coating can be applied to the billet.

The principal reaction that occurs in the lubricating bath may be characterized by the following equation:

$$Zn_3(PO_4)_2 + \text{Na stearate} \rightarrow Na_3PO_4 + \text{Zn stearate}$$

It is known that in order to achieve a satisfactory lubricant coating there must be free acid in the lubricating bath. Conventionally the recommended free acid content of the lubricating bath is such that 0.25 to 0.30 ml. of 0.10 N NaOH neutralizes (to a phenolphthalein endpoint) 10 ml. of the lubricating solution.

Conventionally, this free acid content is maintained by the addition of sulfuric acid, the reaction being characterized as

$$\text{Na stearate} + H_2SO_4 \rightarrow Na_2SO_4 + \text{stearic acid}$$

I have determined, however, that a superior lubricant coating may be achieved if the free acid concentration of the bath is such that 10 ml. of the lubricating solution is neutralized by 0.6 to 0.8 ml. of 0.10 N NaOH. It is obvious that if sulfuric acid were used to maintain this free acid concentration, the salt build-up would be more rapid and the life of the lubricating bath would be extremely short.

I have determined, however, that this free acid content may be maintained by the frequent addition of small quantities of commercial stearic acid. By using stearic acid rather than sulfuric acid I have determined that there is no appreciable salt buildup, that the free acid content can be increased to a more optimum level and that the resulting bath life is greatly increased even over that which was formerly maintained by the lower free acid concentration.

I have discovered that this preferred acidity represents approximately 5% free stearic acid based on the dry solids in the lubricating solution.

Attempts to duplicate this acid concentration by the use of more acid buffers in place of the stearic acid do not give the same effect, probably because of the increased salting out action of the more acid buffering salts.

The following are specific examples of the method of controlling the reaction of the lubricant with the phosphate undercoating. In these specific examples, the free acid content was determined by the following method:

170 ml. of isopropyl alcohol, which has been previously neutralized with 0.10 N NaOH to phenolphthalein endpoint, is placed in a large erlenmeyer flask; 10 ml. of the hot lubricating bath is then added to the alcohol and the resulting mixture boiled gently for two minutes. The solution is then titrated with 0.10 N NaOH to the phenolphthalein endpoint, the free acid content being reported as milliliters of 0.10 N NaOH.

The lubricating bath is also tested for total fats and

fatty acids by use of the Babcock test. In these examples the Babcock reading is obtained by the following method:

20 ml. of the hot lubricating bath is placed in a Babcock bottle with 20 ml. of 50% sulfuric acid. The bottle is then placed on a steam bath until completely reacted (approximately 2 hours). Hot water is then added to the bottle to bring the fatty acids up to scale for reading while the reacted product is still melted. The resulting reading is reported as the Babcock number.

EXAMPLE I

An aluminum ring was cleaned by acid etching and washed with distilled water. The cleaned ring was then placed in a phosphating bath for 3 minutes, the temperature of the bath being maintained at 130° F. The phosphating bath had the following composition:

Phosphating bath

Make-up solution	lbs.	90
H_3BO_3	lbs.	15
$ZnCO_3$	lbs.	0.89
$FeSO_4$	lbs.	2.50
$NaHF_2$	lbs.	0.89
H_2O	gals.	100

Composition of make-up solution

	Weight percent
$Zn(BF_4)_2$	7.8
$Zn(NO_3)_2$	13.8
$Zn(H_2PO_4)_2$	18.7
H_3BO_3	0.5
H_3PO_4	4.7

The coated ring was then dried and after drying was immersed in a vat containing 200 gallons of a lubricating bath having the following composition:

	Weight percent
Na stearate [1] / Na palmitate	50.4
$Na_2CO_3 \cdot 10H_2O$	25.4
$Na_2B_2O_7 \cdot 10H_2O$	2.3
NaOH	0.6
H_2O (free)	21.3
Stearic acid	(see below)

[1] 50–50 mixture.

The temperature of the lubricating bath was maintained at 150° F. and the ring immersed therein for 5 minutes. The ring was then removed from the bath and dried and the resulting lubricant removed from the ring and weighed. It was determined that 0.126 gram of lubricant had been applied to the ring by the process.

The following table illustrates the weight of lubricant per ring obtained as related to the amount of stearic acid added to the lubricating bath. The by weight amount of stearic acid is based on the amount of dry lubricant utilized.

Added stearic acid, percent:	Weight of lubricant per ring, grams
0	0.104
2	0.110
5	0.126
10	0.063
15	0.053

EXAMPLE II

The lubricating bath was prepared using 138 lbs. of a lubricant mixture consisting of

Na stearate [1] / Na palmitate	Wt. percent	50.4
$Na_2CO_3 \cdot 10OH_2O$	do	25.4
$Na_2B_2O_7 \cdot 10H_2O$	do	2.3
NaOH	do	0.6
Stearic acid (62° C. titre)	lbs.	7.5
H_2O	gals.	200

[1] 50–50 mixture.

The Babcock number of the resulting solution was 5.3 and the free acid content was 0.7 ml. of 0.10 N NaOH. A 4-inch pipe billet was cleaned and coated with zinc phosphate in the manner described in Example I. The billet was then dipped into the lubricating bath for 5 minutes, the temperature of the bath being maintained at 150° F. The coating was examined and found to be uniform in thickness and distribution. In addition, some free stearic acid was found in the lubricating film. Additional billets were coated using this lubricating bath.

The following table illustrates the composition of the bath initially and the additions of additional lubricant and stearic acid. In this table Babcock refers to the Babcock test result or number, F.F.A. refers to the free fatty acid in terms of ml. 0.10 N NaOH needed to bring the solution to a phenolphthalein endpoint, Lubricant refers to the mixture of sodium stearate and sodium palmitate and the buffers in the amounts listed at the beginning of Example II, Ft.[2] refers to the square feet of total surface area on the billets lubricated, and H_2O to the amount of water added.

Throughout this experimental run it was attempted to maintain the acid content at between 0.6 and 0.8 ml. of 0.10 N NaOH. Some variation in the acid concentration may well have been caused by experimental error, but I determined that a superior lubricant coating was achieved when the free acid content was maintained in the optimum range of 0.6 to 0.8 ml.

Time	Babcock	F.F.A.	Lubricant, pounds	Stearic Acid, pounds	Ft.[2]	H_2O, gallons
			108	0	0	200
8:50	3.3		30	5	0	
9:45	4.7	.05		1.5	0	
10:30		.2		1.0		
11:00	5.4	.7				
17:00		.8				
18:15	5.6	.75			595.2	
7:20	5.3	.8				
9:45		.8				
11:30		.6				
13:20	5.3	.6				
15:35		1.0				
16:10		1.2				
17:30		1.2				
18:30		1.2				
7:15	4.4	1.1			3,322.68	22
7:45		.6				
8:10		.5				
10:30		.6				
12:40		.7				
13:45	4.1	.6				
16:15		.6			5,758.04	7⅓
7:10	4.2	.5	9	½		
9:25	3.5	.7				
10:30	4.2					
11:20		.7				
11:30		.5				
13:50		.5				
14:10		.6			7,455	14⅔
7:30	3.5	.3	25	1¼		
8:00		.24				
8:30	4.6	.7				
10:20	4.4	.4				
11:00		.4		1		
13:20		.7				
15:05		.6			9,295	7⅓
7:15	4.5	.55		1.0		
9:30	4.7	.7				
12:55		.6				
13:10		.4				14⅔
13:30	4.5	.6			11,331	
7:15	4.0	.3		1.0		5.5
9:30		.7				
11:00		.5				
11:30	3.9		10	0.5		
13:00	4.3	.5				
15:00		.6			13,169	
7:30						5.5
7:40	4.2	.3		¾		
9:20		.5		½		
12:55		.7				
13:30	3.5		20	1		
16:30	4.7	.7			14,169	
Total			202	15	14,169	277

The resulting coated billets were extruded in a conventional Lake Erie 2500-ton horizontal extrusion press having a die, punch-head and mandrel. The starting extrusion temperature was 220° F. It was found that under these conditions the required press pressure was 700 tons.

A control run was made using billets treated in the conventional manner where the free acid of the lubricating bath was maintained with sulfuric acid. The pressure required for these conventional billets was 750 tons. An analysis of the lubricant film on the billets treated in accordance with the present invention showed that the film contained 2.7 percent stearic acid. In these tests the lubricant bath modified in accordance with the present invention consistently treated 15,000 sq. ft. of billet surface before it had to be replaced. Conventional lubricant baths utilizing sulfuric acid as an acid control were exhausted after only 2,000 sq. ft. of billet per bath.

I have discovered that by increasing the free acid content of the bath and utilizing stearic acid in place of sulfuric acid to maintain the free acid, the rate of formation of zinc stearate on the billet was increased thereby shortening the time required in the lubricating bath.

As was demonstrated by an analysis of the lubricating film, some free stearic acid was coprecipitated in the lubricating film. This free stearic acid acted as a binder to the zinc stearate, reducing its tendency to powder off during handling.

I also observed that the free stearic acid either increased the wetting action of the lubricant on the die and billet during extrusion or reacted with the freshly bared aluminum surfaces so as to reduce galling.

Finally, it was found on production tests that the resulting lubricant formed by this method of control resulted in reduction of extrusion pressures by approximately 10%. Any phosphate base lubricant may be improved by my method.

Having fully described my invention, it is to be understood that I do not wish to be limited to the precise details of the examples set forth but my invention is of the full scope of the appended claims.

I claim:

1. In a method for applying a lubricant to a metal billet prior to the cold extrusion thereof, the steps comprising: applying a uniform coating of zinc phosphate to said billet; placing the coated billet in a lubricating bath comprising an aqueous mixture of a water soluble salt of stearic acid and free stearic acid wherein the zinc phosphate coating is converted to a lubricant coating including zinc stearate; and maintaining the free stearic acid concentration of the lubricating bath at a level such that 10 ml. of the bath is neutralized by 0.6 to 0.8 ml. of 0.10 N sodium hydroxide by the addition of stearic acid.

2. In a method for applying a lubricant to a metal billet prior to the cold extrusion thereof wherein the billet is coated with zinc phosphate and the zinc phosphate coating is allowed to react with a water soluble salt of stearic acid in a lubricating bath having a free stearic acid as a constituent thereof, the improvement comprising: maintaining the free stearic acid concentration of the lubricating bath at a level such that 10 ml. of the bath is neutralized by 0.6 to 0.8 ml. of 0.10 N sodium hydroxide by the addition of stearic acid.

References Cited in the file of this patent

Schuster: Abstract of application 37,498, filed July 7, 1948, published Nov. 20, 1951, 652 O.G. 891.