

[54] **SURFACE TREATED STEEL SHEET FOR USE IN A FORMING OPERATION**

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[57]

ABSTRACT

Surface treated steel sheet for use in a forming operation having a layer of a higher alcohol material which is solid at room temperature and of which the major constituent is one or more substances selected from the group consisting of higher alcohols, and, beneath the former layer, a layer of a chemically treated coating film or a layer of coating film of one or more metals selected from the group consisting of Zn, Pb, Cd, Cu, Cr, Sn and Al.

2 Claims, No Drawings

SURFACE TREATED STEEL SHEET FOR USE IN A FORMING OPERATION

This invention relates to a surface treated steel sheet for use in a forming operation, which can be easily lubricated and from which adhering matter can be readily detached.

As lubricants for steel sheet used in a press forming operation, oily lubricants in liquid or paste form have hitherto been used. Recently, however, attempts have been made to apply solid lubricants in which metallic soaps are the major constituent. These lubricants having metallic soap groups are advantageously applied as a preliminary lubricant to a surface treated steel sheet not only because of their better lubricating ability relative to that of oily lubricants but also because of the convenience with which the steel sheet can be handled after the application of the solid lubricants. On the other hand, as they are applied in the form of an aqueous solution, prolonged high temperature heating is required to dry the coating. This leads to the degraded producibility, accelerates aging of the steel sheet and deteriorates the quality of the steel, which also decreases the workability in the forming operation.

As a remedy to cover the drawbacks of the lubricants containing these metallic soaps, the present inventors have developed preliminarily lubrication treated steel sheets, the surface of which is coated first with a metal selected from the group consisting of zinc, copper and cadmium or an alloy thereof and further with a layer of a substance that is solid at room temperature and is composed higher carboxylic acids. A portion of these developments have been published in Patent Publication Sho 44-16774 and Sho 44-20217.

The surface coating material of which a higher carboxylic acid is the main constituent can be applied more easily and is better in lubricating action relative to the coating film of metallic soap. Further, since the said coating material does not require high temperature drying in the treatment, it does not accelerate the aging of the steel sheet and, hence, does not deteriorate the material of the steel sheet itself. However, the coating film can not be removed easily. More particularly, a longer time is required to remove the coating film in the alkali degreasing process than it does with a steel sheet on which anti-rusting oil is applied.

This is presumably due to the higher carboxylic acid which was chemically adsorbed firmly on the plated layer of Zn, Pb, Cd or Cu or the chemically treated coating film, both existing as the primary layer on the steel sheet. This is one of the drawbacks encountered during painting after the press molding process.

The composition for coating is required, on one hand, to have strong adsorptivity to produce a sufficient lubricating property on the surface, for example owing to polar groups contained in the molecules. On the other hand, however, there should be a limitation to the adsorptivity since easy removal of the coating film is also required after the molding process.

On the whole, compounds having a carboxyl group or groups, such as, higher carboxylic acids, which are chemically adsorbed firmly on a plated layer of Pb, Cd or Cu or on a thin layer of chemically treated coating film on the surface of a steel sheet, are not suitable to use for a surface lubricant when the property of easy removal is essential.

The present inventors have recently discovered, as a consequence of various investigations on this problem, that a steel sheet which is first coated with a certain film and then treated with a higher alcohol coating material, which is solid at ambient temperature, meets the requirement.

The higher alcohol application agent has only weak absorbing power to the surface of steel sheet, as is generally recognized, and therefore if a steel sheet, on which the agent has been applied directly on the surface, is treated by the molding process, the lubricating film thus formed can not follow the increase of area as a result of the molding process and may result in burning or bite of the surface. Therefore, the material has not been used as lubricating agent for the molding process.

The metal coatings of this invention to be applied on a steel sheet include the following ones:

1. A coating with a metal selected from the group consisting of Zn, Pb, Cu and Cd, and a coating with an alloy in which the main constituent is one or more metals mentioned above produced by ordinary electroplating; a coating with a metal mentioned above produced by an ordinary molten metal plating method; and a metal coating with which the surface of the steel sheet is converted to an alloy containing iron as an ingredient by a thermal diffusion treatment of any coating mentioned above to form alloy from the metal and the base steel.

2. The chemically treated coating films to be applied to the steel sheet include a layer of hydrated oxide which was obtained by applying anhydrous chromic acid or a phosphate or a mixture thereof in the form of an aqueous solution and a layer of metallic oxide which was deposited from an aqueous solution of chromate, phosphate or a mixture thereof by making the solution contact with the surface of the steel sheet in the presence of chemical reductant or with the combined use of electrolytical cathodic reduction or further a baking treatment.

The steel sheet of this invention is produced by applying on the above mentioned coating films a higher alcohol material which is solid at room temperature and of which the main constituent is one or more substances selected from the group consisting of the higher alcohols described below.

For the higher alcohol materials to be applied, those alcohols containing at least 12 carbon atoms in the molecule which becomes solid after being applied at the room temperature are preferred. They include, for example, dodecanol, tetradecanol, hexadecanol and octadecanol.

Admixing a rust preventure agent, a coloring material and a filler to the higher alcohol material to such an extent as not to alter the fundamental properties of the material does not spoil the effect of the steel sheet of this invention.

The ways in which the higher alcohol materials which are solid at the room temperature are applied to the surface of steel sheets include applying in liquid form, either made molten by heating or in the form of a solution in an organic solvent, with rollers, spray, brush or by dipping or streaming, onto the surface of the steel sheet followed by heating with an infrared light or hot air to fuse the material and form a uniform layer on the surface.

In applying a metal coating of Zn, Pb, Cd or Cu on the steel sheet base, uniform application of the said higher alcohol materials and excellent workability in the forming operation can be attained for the applied amount more than 250 mg/m² when one of the metals is applied along and more than 250 mg/m² as the total amount of the said metals when an alloy coating is applied. As the amount of the metal coating is increased further, the lubrication effect of the higher alcohol materials is improved even more until the total amount of the metal coating reaches 2500 mg/m², and the lubrication effect remains constant for an amount of metal coating over 2500 mg/m². Therefore, the amount of the metal coating of this invention should be preferably more than 250 mg/m².

The amount of the chemically treated coating film to be formed either directly on the surface of steel sheet or on the metal coating of the above mentioned metals and Cr, Sn and Al should be preferably more than 300 mg/m² when a chemically treated coating film of hydrous oxide or hydrated metal oxide is formed from an aqueous solution of phosphate. For an amount less than 300 mg/m², not only the coating film itself but also the higher alcohol materials applied on it become nonuniform, which means the lowered ability in lubrication. Thus, an amount larger than 300 mg/m² is desired.

On the other hand, when the chemically treated coating film of hydrous oxide or hydrated metal oxide is formed from an aqueous solution of chromate, an amount larger than 50 mg/m² is desired. The lubricating ability is increased with an increase in the amount of coating film, but for an amount less than 50 mg/m², sufficient lubricating ability is not attained for practical purposes.

In the case where an aqueous solution containing both anhydrous chromic acid and phosphate is applied, an amount of the coating film larger than 50 mg/m², the same as with the chromate treatment, is desired.

The higher alcohol material that is solid at the room temperature produces an appreciable effect even when it is applied in a small amount, but a remarkable effect when applied in an amount larger than 50 mg/m². The effect on the lubricating ability is increased with an increase of the applied amount, but the upper limit may be set to 5 mg/m² in practical application to the steel sheet of this invention, considering the accumulated adhesion of the material to rollers and the mold for forming, transfer of the adhering material to the steel sheet, time required to remove it and the contamination of wash liquid.

The steel sheets of this invention include, in addition to the steel sheets on which the surface treatment of this invention is applied on the whole surface of both sides, those steel sheets on which the surface treatment is applied on the whole surface of a single side or on a part of a single or both sides. The latter treatment may be suitable depending on the forming operation.

The steel sheets of this invention are produced from the following three stages of operation: production of the steel sheet (non-lated), application of the specified coating film on the steel sheets and application of the higher alcohol materials. These three stages of operation are not necessarily performed in a factory, but the higher alcohol material may be applied, for example, in the blanking line or immediately before pressing in the pressing operation.

A steel sheet, as well as a cut sheet therefrom, which is produced in the way described above belongs to the present invention.

Advantages of the steel sheets of this invention will be described as follows:

1. Easy removal of the preliminary lubricant

The preliminary lubricant can be easily removed with an alkaline degreasing agent or an organic solvent. The adhesive power of the higher alcohol material to the specified coating film of this invention is so weak as not to cause troubles in the forming operation in contrast to the corresponding material of carboxylic acid, and the former can be removed more easily than the latter. In addition, the small amount of the former material to be applied reduces contamination of the remover solution.

2. Excellent rust preventing ability

Since the surface of the steel sheets is covered by the coating layer consisting of the specified coating film and the higher alcohol material, the surface is effectively protected from rust formation, and therefore application of oil for rust prevention is not required while the higher alcohol material exists on the surface.

3. In contrast to the difficultly drying water-soluble lubricants such as ordinary metallic soap lubricants, the higher alcohol material to be applied can be made molten by heating or may be applied on the surface of steel sheet in the form of a solution in an organic solvent, the material dries easily and a short time heating suffices if necessary, so that deterioration of the steel sheet does not occur and high producibility can be achieved.

4. The steel sheets of this invention on which the specified coating of chemically treated film is applied can be subjected to removal of the higher alcohol material after the forming operation and then to painting without treating the base surface, so that the producibility and the cost can be improved.

5. In the steel sheets of this invention on which the specified metal coating is applied, the higher alcohol material is removed after the forming operation is completed and then the metal coating of zinc or cadmium is finally removed by acid treatment. In the acid treatment, the metal coating of zinc or cadmium is dissolved in the acid solution acting as electrolytical anode against the steel base. As a result, the finally exposed surface of the steel base is extremely active as it is when treated cathodically with an acid solution, and therefore it forms a very good base for permanent plating. When the steel sheets of this invention are employed for such use, thin coating films of zinc or cadmium are preferred for economy and easy removal, that is, the total amount of zinc and cadmium in the film is 250 - 2500 mg/m². These coating films are also useful as preliminary coating films on which to form a uniform layer of a chemically treated coating of phosphate.

6. No difference from untreated steel sheets in weldability.

The steel sheet of this invention shows no difference from untreated uncoated steel sheets with respect to welding strength, and marks and stains by a welding machine.

7. Excellent workability in forming operation

Although the lubrication effect of coating films of higher carboxylic acids is generally recognized as is published in Patent Publication Sho 44-16774 and Sho 44-20217, the lubrication effect of the coating film of higher alcohol materials is no less excellent, so that a

further application of a lubricating oil is not required. This leads to improved workability in the press forming operation and lowers the rejection rate.

8. Since the surface of the steel sheet of this invention is solid at room temperature, it is not sticky and does not become dirty. Due to the small amount of the higher alcohol material to be applied, the material does not drift or flow and does not transfer to another sheet when some sheets are piled. Thus, handling of the sheets is easier than of steel sheets to which rust preventing oil is applied.

EXAMPLE 1

Various coating materials and preliminary lubrication treatments relating to this invention as shown in Table 1 were applied on cold rolled rimmed steel sheets with a thickness of 0.8 mm, and the press forming test was conducted. Results are shown in Table 2.

As is evident in Table 1 and 2, the steel sheets of this invention were more easily workable in the forming operation than those of the conventional art and of comparison runs under any surface treatment condition, since CCV the was lower by more than 0.8 mm and ErV was higher by approximately more than 1 mm.

EXAMPLE 2

The chemically treated coating films as described in Table 3 were applied on the surface of cold rolled rimmed steel sheets of 0.8 mm thickness (both plated and unplated steel sheets), and a higher alcohol material was applied as examples of this invention. For comparison purposes, commercial press oil was applied as examples of previous treatments. The final products were compared with respect to the workability. Results thereof are shown in Table 4.

TABLE 1

Num- ber	Coating to steel base			Higher alcohol or lubricating oil		
	Material	Method of application	Amount (g./m. ²)	Material	Amount (g./m. ²)	
This invention	1 Phosphate	Spraying	0.5	Hexadecanol	0.3	
Conventional	2 do	do	0.5	Commercial press oil	6	
This invention	3 Chromate	Electrolysis	0.5	Hexadecanol	0.3	
Conventional	4 do	do	0.5	Commercial press oil	6	
This invention	5 Zinc	Electroplating	5	Hexadecanol	0.3	
Conventional	6 do	do	5	Commercial press oil	6	
This invention	7 Lead	do	5	Hexadecanol	0.3	
Conventional	8 do	do	5	Commercial press oil	6	
This invention	9 Copper	do	5	Hexadecanol	0.3	
Conventional	10 do	do	5	Commercial press oil	6	
This invention	11 Cadmium	do	5	Hexadecanol	0.3	
Conventional	12 do	do	5	Commercial press oil	6	
This invention	13 Copper-zinc	do	6.5-2.5	Hexadecanol	0.3	
Conventional	14 do	do	6.5-2.5	Commercial press oil	6	
This invention	15 Zinc-tin	do	5.5-4.5	Hexadecanol	0.3	
Conventional	16 do	do	5.5-4.5	Commercial press oil	6	
Present	17 Zinc	Molten plating	100	Hexadecanol	0.3	
Conventional	18 do	do	100	Commercial press oil	6	
Present	19 Lead-tin	do	80-20	Hexadecanol	0.3	
Conventional	20 do	do	80-20	Commercial press oil	6	
Present	21 Zinc-iron	Molten zinc plating plus thermal diffusion	50-6	Hexadecanol	0.3	
Conventional	22 do	do	50-6	Commercial press oil	6	
Present	23 Zinc-phosphate	Electroplating plus spraying	5-1	Hexadecanol	0.3	
Conventional	24 do	do	5-1	Commercial press oil	6	
Present	25 Copper-chromate	Electroplating plus dipping	5-0.5	Hexadecanol	0.3	
Conventional	26 do	do	5-0.5	Commercial press oil	6	
Do	27 No treatment	do		do	6	
Comparison	28 do	do		Hexadecanol	0.3	
Do	29 Zinc	Electroplating	5	Vaseline	5	

REMARKS.—Present: Present invention; Conventional: Conventional treatment; Comparison: For comparison.

TABLE 2

	No.	CCV (mm.)	ErV (mm.)		No.	CCV (mm.)	ErV (mm.)
Present	1	37.0	12.2	Present	15	36.7	12.4
Conventional	2	38.1	11.0	Conventional	16	37.9	11.6
Present	3	36.8	12.5	Present	17	37.2	12.0
Conventional	4	38.2	11.2	Conventional	18	38.0	10.9
Present	5	36.5	12.3	Present	19	36.1	12.4
Conventional	6	37.6	11.5	Conventional	20	37.3	11.0
Present	7	36.3	12.4	Present	21	37.0	12.2
Conventional	8	37.4	11.6	Conventional	22	37.8	11.2
Present	9	36.4	12.2	Present	23	36.7	12.0
Conventional	10	37.2	11.3	Conventional	24	37.8	10.8
Present	11	36.6	12.3	Present	25	36.3	12.9
Conventional	12	38.1	11.2	Conventional	26	37.5	11.8
Present	13	36.4	12.6	Conventional	27	37.9	11.3
Conventional	14	37.5	11.6	Comparison	28	37.6	11.4
				Comparison	29	38.2	10.7

REMARKS.—CCV: Conical cup value, blank diameter of the spherical top punch 50 mm. ϕ ErV: Limit in expansion height, using a flat top punch 40 mm. ϕ in diameter having large diameter shoulder, flange restricted.

TABLE 3

	Plating		Chemically treated coating film		Amount (g./m. ²)	Applied higher alcohol material (or lubri- cating oil)	Amount (g./m. ²)
	Material	Amount (g./m. ²)	Material	Method of application			
Examples of this invention:							
A	No plating		Hydrous chromic oxide.	Cathodic electrolysis in a chromate solution	100	Hexadecanol	0.5
B	do		A mixture of hydrous chromic oxide and phosphorus oxide.	Cathodic electrolysis in a solution containing phosphate and chromate.	30	do	0.5
C	do		Hydrous chromic oxide.	Application of a solution containing phosphate and anhydrous chromic acid.	50	do	0.5
D	do		do	Dipping in a solution of chromate	50	do	0.5
E	Zn	1	do	Cathodic electrolysis in an aqueous solution of chromate.	100	do	0.5
Examples of conventional treatment:							
F	Zn	1	Phosphate	Spraying an aqueous solution of phosphate	500	do	0.5
G	No plating		Hydrous chromic oxide.	Cathodic electrolysis in an aqueous solution of chromate.	100	Commercial press oil.	5
H	Zn	1	do	Dipping in an aqueous solution of chromate	60	do	5

TABLE 4

Examples of this invention	A	CCV (mm) 36.7	ErV (mm) 11.2	25	Examples of conven- tional treatment	I	Application of rust preventing oil	2
Examples of conventional treatment	B	36.4	11.4	30	J	J	Application of machine oil No 120	3
	C	37.0	11.0		K	K	Application of commercial press oil	6
	D	36.9	11.1		L	L	The same as in A on a chromate coating film	0.2
	E	36.3	11.7		M	M	The same as in B etc.	1
Examples of conventional treatment	F	36.0	11.9	35	N	N	The same as in G etc.	0.2
	G	37.9	10.3		O	O	The same as in H etc.	1
	H	38.2	9.8		P	P	The same as in I etc	2
					Q	Q	The same as in K etc.	6

As seen in the table, the present invention exhibits excellent workability in the forming operation.

EXAMPLE 3

Steel sheets of this invention were prepared by electro-plating lead in the amount of 1 g/m² on rimmed steel sheets of 0.8 mm thickness and treating the surface as shown in Table 5. Tests of workability in the forming operation and of removal of the treating agent were conducted with specimens prepared from the steel sheets of this invention, the previous treatment and the comparison runs. Results thereof are shown in Table 6.

TABLE 5

	Treatment	Amount applied as non-volatile matter (g/m ²)	50	55	60	65
Examples of this inven- tion	A	Application and drying in a perchloroethylene solution of tetradecanol	0.2	1	0.2	1
	B	Application and drying in a perchloroethylene solution of 60% tetradecanol and 40% dodecanol	0.2			
	C	Application and drying in a perchloroethylene solution of hexadecanol	0.2			
	D	do.	1			
Examples for compari- son	E	Application and drying in a perchloroethylene solution of octadecanol	0.2	1	0.2	1
	F	Application and drying in a perchloroethylene solution of 60% octadecanol and 40% hexadecanol	1			
	G	Application and drying in a perchloroethylene solution of palmitic acid	0.2			
	H	do.	1			

TABLE 6

		Workability		Time required for removal (sec)		
		CCV (mm)	ErV (mm)	Spray de-greasing	Dipping de-greasing	
40		A	36.7	12.0	5	10
		B	36.3	12.4	10	60
45	Examples of this invention	C	36.7	12.1	5	10
		D	36.2	12.5	10	60
		E	36.4	12.1	5	10
		F	36.0	12.6	10	60
	Examples for comparison	G	37.0	12.4	10	120
		H	36.6	12.7	60	300
50	Examples of conventional treatment	I	38.5	10.8	10	60
		J	38.7	10.7	30	120
	Examples of this invention	K	38.0	11.4	30	180
		L	36.9	12.2	10	30
55	Examples for comparison	M	36.3	12.6	30	60
		N	37.2	12.1	30	120
	Examples of conventional treatment	O	36.8	12.6	120	> 600
		P	38.4	10.7	30	120
60		Q	38.0	11.5	180	>600

CONDITIONS FOR TESTING

Test of workability: No lubricant was applied except as mentioned above.

Test of time required for removal: 10 g/l of "Perco-cleaner" No. 364S

Spray degreasing: Spraying of 60°C aqueous solution of the above degreasing agent

Dipping degreasing: Dipping in a 60°C aqueous solution of the above degreasing agent (with agitation of the solution)

Time required: Time required before complete wetting was attained was measured.

As is readily seen in the table, the present invention offers much more excellent removal relative to the comparison and very excellent workability in comparison with the conventional treatment.

EXAMPLE 4

Tests of workability were conducted with the steel sheets which were prepared by electroplating zinc in the amount of 10 g/m² on cold rolled rimmed steel sheets of 0.8 mm thickness and then applying several different amounts of octadecanol in a perchloroethylene solution. Results are shown in Table 7.

TABLE 7

Amount of octadecanol applied (mg/m ²)	CCV (mm)	ErV (mm)
0	39.0	9.8
10	38.8	10.0
50	37.8	10.9
200	37.2	11.7
500	36.8	12.0
1000	36.5	12.2
5000	36.1	12.4

As is apparent in the table, the workability was improved with the increase of the applied amount, and this is especially remarkable for the amount larger than 50 mg/m².

EXAMPLE 5

Tests of workability were conducted with the steel sheets which were prepared by electrolytically applying coating films of chromate of several different thickness on cold rolled rimmed steel sheets of 0.8 mm thickness and then applying on the surface 0.5 g/m² of hexadecanol by hot melting followed by rolling. Results thereof are shown in Table 8.

TABLE 8

Coating film of chromate applied (mg/m ²)	CCV (mm)	ErV (mm)
0	37.5	10.5
20	37.2	10.7
50	36.7	11.9
200	36.4	12.2
500	36.2	12.6
2000	36.5	12.3

As is readily seen in the table, the workability was improved with the increase of the amount of applied chromate coating film, and this inclination becomes remarkable for the amounts exceeding 50 mg/m² of the coating film.

EXAMPLE 6

Tests of workability were conducted with the steel sheets of this invention, A through G, which were pre-

pared by applying several different amounts of copper plating on cold rolled rimmed steel sheets of 0.8 mm thickness and further applying on them a toluene solution of hexadecanol to such an extent as to form a layer of non-volatile matter of 0.3 g/m², and with the steel sheets of previous treatment, H and I. Results are shown in Table 9.

A : Steel sheet on which 10 mg/m² of copper was plated

B : " 100 mg/m² "

C : " 250 mg/m² "

D : " 500 mg/m² "

E : " 2 g/m² "

F : " 10 g/m² "

G : " 50 g/m² "

H : (Previous treatment) The same material as in C on which commercial press oil was applied.

I : (Previous Treatment) The same material as in A on which commercial press oil was applied.

TABLE 9

	Amount of copper plate	CCV (mm)	ErV (mm)
A	10 mg/m ²	38.5	10.3
B	100	38.4	10.3
C	250	37.4	11.1
D	500	37.1	11.4
E	2 g/m	36.4	12.0
F	10	36.5	11.8
G	50	36.3	11.9
H	250 mg/m ²	38.2	10.6
I	10	38.8	10.1

A-G: Examples of this invention

H and I: Examples of conventional treatment

As is seen in the table, workability was improved with the examples of this invention, C through G, for which the amount of copper plated was larger than 250 mg/m², but, as the amount exceeded 2 g/m², the improvement became rather sluggish. In contrast, the workability of the conventional treatment, H and I, was inferior to that of C and A, respectively, in which the same amounts of copper were plated.

What is claimed is:

1. A surface treated steel sheet suitable for use in a forming operation which comprises a steel sheet having thereon a top layer of an alcohol having at least 12 carbon atoms, which alcohol is a solid at room temperature, and interposed between the alcohol layer and the steel sheet, a layer of a metal selected from the group consisting of Zn, Pb, Cu, Cr, Cd, Sn, Al, and alloyed combinations thereof.

2. A surface treated steel sheet suitable for use in a forming operation which comprises a steel sheet having thereon a top layer of an alcohol having at least 12 carbon atoms, which alcohol is a solid at room temperature, and interposed between the alcohol layer and the steel sheet, a layer of a hydrated oxide or a metallic oxide.

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