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(54) STAINLESS STEEL SHEET COVERED WITH ALKALI-SOLUBLE PROTECTIVE COAT

(57) A stainless steel sheet having on its surface a protective film for protecting the surface of the stainless steel sheet when worked by pressing. The protective film is comprised of a lower-layer coating film and an upper-layer coating film which are successively formed on its surface, the former being formed of an epoxy-modified acrylic resin obtained by modifying an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 0°C to 20°C with an epoxy oligomer having a molecular weight of from 500 to 2,000, to a degree of from 3% by mass to 20% by mass, and the latter being formed of an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 40°C to 80°C; the upper- and lower-layer coating films having a total thickness of from 1 µm to 20 µm.

Description

TECHNICAL FIELD

This invention relates to a protective-film coated stainless steel sheet whose protective film exhibits a superior resistance to dragging (or scoring) when worked by pressing, and moreover can be removed with an alkali solution after the pressing.

BACKGROUND ART

Stainless steel sheets have so good corrosion resistance and appearance that they are used for many purposes with their surface texture as they are, as seen in kitchen implements, construction materials and so forth. Such stainless steel sheets, however, have a disadvantage that any change having once occurred in the surface state tends to be very conspicuous even when it is partial. Accordingly, when, e.g., members that utilize the surface texture of a stainless steel sheet as it is are produced by pressing, a protective film formed of vinyl chloride resin is stuck on the surface in order to prevent dragging, a phenomenon in which the steel sheet surface abrades because of its friction with a mold. Also, since the protective film formed of vinyl chloride resin has insufficient lubricity and workability, the stainless steel sheet is worked while applying a press oil on the protective film, and, after protective films are manually peeled, the surfaces of products obtained by working are washed with a chlorine type solvent such as trichloroethane or an aqueous alkali solution

However, because of the insufficient lubricity of the protective film formed of vinyl chloride resin, film cuts may partly occur when the stainless steel sheet is worked by pressing, tending to cause the dragging on the steel sheet surface. Also, it takes much labor, time and cost to manually peel protective films. In addition, since the part having been drawn by working comes in firm adhesion to the stainless steel sheet, the films may break when peeled or can not be peeled to remain at some portions. Accordingly, in order to prevent as far as possible the films from cutting when peeled, the protective film is formed in a large thickness, where the protective film must be formed in a large thickness even when members not so severely worked by pressing are produced, resulting in a high material cost. Also, application of the press oil and removal thereof cause a bad operating environment.

Accordingly, in order to solve such problems, a method is proposed in which, in place of the protective film formed of vinyl chloride resin, an aqueous solution or aqueous dispersion comprised of an alkali-soluble resin composition chiefly composed of acrylic resin is coated on the stainless steel sheet to provide a protective film formed of acrylic resin. The stainless steel sheet on which the protective film has been formed by this method is worked into members and thereafter the members obtained are treated with an alkali solution to dissolve protective films to thereby remove them, and hence it is unnecessary to peel the protective films. Thus, the protective film can be formed on the stainless steel sheet in the state the former firmly adheres to the latter so as not to cause peeling when worked by pressing, and not to cause the dragging. Also, since protective films are entirely dissolved by the alkali solution, the protective films may by no means remain unremoved.

This alkali-soluble composition is a composition made soluble in alkali by adjusting the acid value of an acrylic resin. Its adhesion to articles to be protected is known to be controlled by a method of controlling it in accordance with glass transition temperature of the acrylic resin or by a method of controlling it by modifying the acrylic resin with an oligomer or prepolymer of a different resin. As an example in which a composition whose adhesion is improved by controlling the glass transition temperature is used to form the protective film of a stainless steel sheet, there is known a stainless steel sheet on the surface of which a lower-layer coating film of from 1 μm to 60 μm thick, formed of an acrylic resin having an acid value of from 40 to 400 and a glass transition temperature of from -10°C to 30°C, and an upper-layer coating film of from 3 μm to 60 μm thick, formed of an acrylic resin having an acid value of from 40 to 400 and a glass transition temperature of from 40°C to 80°C are successively formed, and the upper- and lower-layer coating films have a total thickness of from 5 μm to 100 μm (Japanese Patent Application Laid-open No. 8-156177).

If a single-layer coating film is made to have a higher adhesion and a higher solubility in alkali, the film may become highly sticky to cause blocking when stainless steel sheets are piled up, and also the stainless steel sheet may show an insufficient resistance to dragging when worked by pressing. Hence, in the above protective film, the lower-layer and upper-layer coating films are made alkali-soluble, and in that state the lower-layer coating film is made to have a glass transition temperature lower than the upper-layer coating film so that the adhesion to the stainless steel sheet can be improved. However, because of still insufficient adhesion and strength of the film, the stainless steel sheet may cause the dragging when severely worked by pressing. Also, since the protective film is removed after the pressing and is thrown away, it is economically preferable to make the film thickness smaller, but because of a low film strength it has been difficult to make the thickness smaller than 5 μm.

Meanwhile, as an example of a composition in which the acrylic resin is modified with an oligomer or prepolymer of a different resin to improve adhesion, an acryl-urethane resin is known which is obtained by allowing an acrylic resin to react with a prepolymer having at least one active isocyanate group and a blocked isocyanate group in the molecule to produce an acrylic resin containing a blocked isocyanate, followed by addition of water and thereafter addition of an amino group-containing compound to react with the acrylic resin containing a blocked isocyanate (Japanese Patent Application Laid-open No. 4-328173). However, when this composition is applied to form the protective film of stainless steel sheet, no uniform coating film can be formed in the case of coating films with a thickness smaller than 3 µm, and hence it has been necessary to form coating films in a larger thickness. For this reason, the composition must be used in a large quantity per unit area, resulting in an increase in the cost for the protective film.

An object of the present invention is to provide an alkali-soluble protective-film coated stainless steel sheet improved in adhesion of the protective film so as to cause no dragging even when worked by severe pressing.

Another object of the present invention is to provide an alkali-soluble protective-film coated stainless steel sheet that may cause no dragging in the stainless steel sheet even when the film is formed in a small thickness.

Still another object of the present invention is to provide an alkali-soluble protective-film coated stainless steel sheet having a uniform coating film even when it is formed in a thin film of 3 µm or less.

DISCLOSURE OF THE INVENTION

The protective-film coated stainless steel sheet of the present invention comprises a stainless steel sheet and successively formed on its surface i) a lower-layer coating film formed of an epoxy-modified acrylic resin obtained by modifying an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 0°C to 20°C with an epoxy oligomer having a molecular weight of from 500 to 2,000, to a degree of from 3% by mass to 20% by mass, and ii) an upper-layer coating film formed of an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 40°C to 80°C; the upper- and lower-layer coating films having a total thickness of from 1 µm to 20 µm.

In order to impart the coating film adhesion and alkali-solubility to the protective film, it is advantageous to make the protective film have a double-layer structure as disclosed in Japanese Patent Application Laid-open No. 8-156177. Accordingly, the present inventors made various studies in order to improve the resistance to dragging when worked by pressing. As a result, they have discovered that the resistance to dragging is improved when the acrylic resin is epoxy-modified. Table 1 shows results obtained when epoxy-modified acrylic resins obtained by allowing an acrylic resin having an acid value of 100 and a glass transition temperature of 10°C, synthesized by copolymerisation of methyl methacrylate, butyl acrylate and methacrylic acid, changing the proportion of the respective components, to react with epoxy oligomers having different molecular weights were coated on the surface of stainless steel sheets, followed by drying, and the coating films formed were tested to examine their dissolution by an aqueous alkali solution, the coating film adhesion, the resistance to dragging and the resistance to blocking. As is seen therefrom, the resistance to dragging is improved when epoxy-modified acrylic resins modified with epoxy oligomers having molecular weights of from 500 to 2,000 are used. The coating film properties shown in Table 1 are tested and evaluated by the methods described later in Example 1.

Table 1

No.	Epoxy oligomer		Coating film		Dragging resistance	Blocking resistance
	Molecular weight	Degree of modification	solubility	adhesion		
1	400	20	A	A	B	B
2	500	20	A	AA	A	B
3	800	3	AA	AA	A	B
4	800	20	A	AA	A	B
5	1,000	1	AA	A	B	B
6	1,000	3	AA	AA	A	B
7	1,000	5	AA	AA	A	B
8	1,000	10	AA	AA	A	B
9	1,000	15	A	AA	A	B

Table 1 (continued)

No.	Epoxy oligomer		Coating film		Dragging resistance	Blocking resistance
	Molecular weight	Degree of modification	solubility	adhesion		
10	1,000	20	A	AA	A	B
11	1,000	25	C	AA	A	B
12	1,200	3	AA	AA	A	B
13	1,200	10	AA	AA	A	B
14	1,600	3	A	AA	A	B
15	2,000	3	A	AA	A	B
16	2,400	3	C	AA	A	B

Remarks:
(1) The degree of modification with epoxy oligomer is indicated as % by mass.
(2) Coating films are in a thickness of 10 µm each.

In the present invention, based on the foregoing findings, the upper- and lower-layer coating films are both formed using materials having large acid values as in the conventional cases, the lower-layer coating film is formed of an epoxy-modified acrylic resin having a lower glass transition temperature, having been modified to a degree of from 3 to 20% by mass, and the upper-layer coating film is formed of an acrylic resin having a higher glass transition temperature, to thereby harmonize the solubility in aqueous alkali solution of coating films, the resistance to dragging and the resistance to blocking.

In the present invention, the lower-layer coating film is a film formed of an epoxy-modified acrylic resin obtained by modifying an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 0°C to 20°C with an epoxy oligomer to a degree of from 3 to 20% by mass. The acid value is defined to be from 40 to 300 because, if it is less than 40, it becomes difficult to remove the coating film by dissolution with an aqueous alkali solution and, if it is more than 300, the coating film strength may lower to cause a possibility that the coating films are scraped off when worked. In order to harmonize the alkali-solubility and the coating film strength, the acid value may preferably be set within the range of from 100 to 300. Here, the acid value refers to the milligram number of potassium hydroxide that is necessary to neutralize a free fatty acid contained in 1 g of the acrylic resin solution. The glass transition temperature is defined to be from 0 to 20°C because, if it is lower than 0°C, the coating film may have an insufficient strength at room temperature to cause a lowering of resistance to dragging, and, if it is higher than 20°C, no high adhesion can be obtained. Also, the resistance to blocking can be more improved when the acrylic resin has a glass transition temperature of from 10 to 20°C.

The molecular weight of the epoxy oligomer used for modifying the acrylic resin is defined to be from 500 to 2,000 because, if it is less than 500, the resistance to dragging may be unsatisfactory, and, if it is more than 2,000, the alkali-solubility may be damaged. The degree of epoxy-modification is defined to be from 3 to 20% by mass because, if it is less than 3% by mass, no sufficient resistance to dragging can be obtained, and, if it is more than 20% by mass, the alkali-solubility may be damaged. In order to harmonize the resistance to dragging and the alkali-solubility, the epoxy oligomer may preferably have a molecular weight of from 800 to 1,200 and be modified to a degree of from 3 to 10% by mass.

Various methods are available as methods by which the acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 0 to 20°C is modified with the epoxy oligomer having a molecular weight of from 500 to 2,000, to a degree of from 3 to 20% by mass. The methods can be typified by a method in which first the acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 0 to 20°C is synthesized and then the epoxy oligomer having a molecular weight of from 500 to 2,000 is added, where an amine is added and thereafter the mixture obtained is heated to about 100°C to allow carboxyl groups of the acrylic resin to react with epoxy groups of the epoxy oligomer, and a method in which epoxy groups of the epoxy oligomer is allowed to react with a carboxyl compound having an unsaturated bond, e.g., acrylic acid, methacrylic acid, maleic anhydride or an unsaturated fatty acid, followed by polymerization while dropwise adding an acrylic monomer.

The upper-layer coating film is formed using an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 40°C to 80°C. The acid value is defined to be from 40 to 300 for the same reason as in the case of the lower-layer coating film. Meanwhile, the glass transition temperature is defined to be from 40°C to 80°C because, if it is lower than 40°C, the coating film may also become sticky when temperature rises in the summer season where the temperature in factories may rise to about 40°C, and, if it is higher than 80°C, the coating film may become brittle and may crack or peel when films are formed.

If the lower-layer coating film and upper-layer coating film have a total thickness smaller than 1 µm, the steel sheet surface can not be prevented from dragging when worked by pressing. If they have a total thickness larger than 20 µm, the coating films may be scraped off by a mold in a very large quantity, so that the mold may have to be frequently repaired, resulting in a lowering of productivity. Hence, they may preferably have a total thickness of from 1 to 20 µm, and more preferably from 1 to 5 µm. When the lower-layer coating film has a lower glass transition temperature, the upper-layer coating film may be made to have a thickness larger by at least 1/2 of that of the lower-layer coating film, whereby the resistance to dragging can be improved.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a draw-bead testing mold used in a coating film dragging resistance test made in Example 1.

BEST MODES FOR WORKING THE INVENTION

The acrylic resins used in the lower-layer and upper-layer coating films may be polymers or copolymers of acrylic acid and/or methacrylic acid or copolymers of any of these monomers with an acrylate, a methacrylate or the like optionally added, the acid value and glass transition temperature of which have been controlled by the degree of polymerization and the components of copolymerization. Here, the acrylate or methacrylate may include methyl acrylate or methacrylate, ethyl acrylate or methacrylate, butyl acrylate or methacrylate, and 2-ethylhexyl acrylate. The copolymerization monomers may be further copolymerized with monomers copolymerizable with acrylate or methacrylate, as exemplified by styrene, acrylonitrile, acrylamide, butadiene and vinyl acetate.

To the upper-layer coating film, a high-polymer resin powder may be added as a lubricant. This brings about an improvement in lubricity to enable working without application of oil, so that an oiling step and a degreasing step can be omitted and also the resistance to dragging can be improved. If, however, the resin powder is added in an amount less than 1% by mass, the lubricity may be poorer than the case when press oil is applied, and if added in an amount more than 25% by mass, the powder may be dispersed in a treating solution with difficulty to form a gel. Hence, the resin powder may be added in an amount of from 1 to 25% by mass, and preferably from 1 to 10% by weight taking account of long-term stability of the treating emulsion. If the resin powder has an average particle diameter smaller than 0.1 µm, the coating film can have a smaller coefficient of friction, but can not have so much lubricity. If it has an average particle diameter larger than 10 µm, the resin powder may come off when worked and can exhibit no lubricity. Hence, the powder resin may have an average particle diameter of from 0.1 to 10 µm.

The resin powder may include, but not particularly limited to, powders of fluorine resins, polyethylene resins or polyester resins. Any of these resin powders may be used alone or in combination, or may be melt-blended. In order to improve the lubricity of coating films, a fluorine resin powder having a good lubricity and a polyethylene resin powder that may deform with difficulty under a high surface pressure may preferably be used in the form of a mixture.

To form the lower-layer and upper-layer coating films on the surface of the stainless steel sheet, an emulsion of the epoxy-modified acrylic resin may be coated by a coating process that can form a uniform coating film, e.g., roll coating, followed by drying, and thereafter an emulsion of the acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 40°C to 80°C may be similarly coated thereon, followed by drying.

EXAMPLES

Example 1

A plurality of treating emulsions of acrylic resins having different acid values and glass transition temperatures were prepared by copolymerizing methyl methacrylate, butyl acrylate and methacrylic acid, changing the proportion of the respective components. Thereafter, among these, those having lower glass transition temperatures were allowed to react with bisphenol-A epoxy oligomers so as to be epoxy-modified. Next, emulsions of the epoxy-modified acrylic resins thus obtained were each coated on the surface of a stainless steel sheet (steel type: SUS304; finished: BA; sheet thickness: 0.6 mm) by means of a bar coater, followed by drying in an oven to form a lower-layer coating film. Thereafter, acrylic resins having glass transition temperatures higher than the acrylic resins having not been epoxy-modified were each similarly coated on the lower-layer coating film, followed by drying to form an upper-layer coating film. The coated stainless steel sheets thus obtained, having acrylic resin coating films, were as shown in Tables 2 and 3.

Then, these steel sheets were examined on the following properties. Results obtained are shown in Table 4.

(1) Solubility of coating films:

Test pieces were immersed in an aqueous NaOH solution (pH: 12; liquid temperature: 40°C), and those which took less than 2 minutes until their coating films completely dissolved were evaluated as "A"; from 2 minutes to less than 5 minutes, as "B"; and 5 minutes or more, as "C".

(2) Coating film adhesion:

Test pieces were subjected to a Du Pont impact test (drop height of a weight: 500 mm; weight of the weight: 500 g), and to a taping test in which a cellophane tape was once stuck to convex portions and then peeled. Those having a coating film retention of 80% or more were evaluated as "AA"; from 60% to less than 80%, as "A"; from 40% to less than 60%, as "B"; from 20% to less than 40%, as "C"; and less than 20%, as "CC".

(3) Resistance to dragging:

Test pieces (30 mm x 250 mm) were subjected to a draw-bead test as shown in Fig. 1 (pressure applied: 1,500 N; draw rate: 8.3×10^{-2} m/sec). Those having a coating film retention of 80% or more at the tested portions were evaluated as "AA"; from 60% to less than 80%, as "A"; from 40% to less than 60%, as "B"; from 20% to less than 40%, as "C"; and less than 20%, as "CC".

(4) Resistance to blocking:

Test pieces were superposed in the manner that their protective film sides were put together, and were left to stand for 24 hours at a temperature of 40°C under application of a pressure of 1,200 N/cm^2. Test pieces naturally separated thereafter were evaluated as "AA"; those which were forcedly separated and in which coating films did not peel, as "A"; those in which coating films partly peeled, as "B"; those in which coating films wholly peeled because of blocking, as "C".

Table 2

Sample No.	Lower-layer coating film				
	Acrylic resin		Molecular weight of epoxy oligomer	Epoxy modification (mass %)	Thickness (µm)
Acid value	Glass transition temp. (°C)				
Example					
1	100	0	1,000	10	5
2	100	10	1,000	3	0.5
3	100	20	2,000	15	2
4	200	20	800	10	4
5	300	10	1,000	20	4
6	300	20	1,200	5	10
7	40	0	500	20	6
8	40	10	800	10	10
Comparative Example					
1	100	10	-	-	10
2	100	0	2,000	25	0.2
3	100	10	2,400	1	10
4	35	10	400	20	5
5	100	30	2,000	20	6
6	400	10	1,000	10	5
7	100	20	2,000	10	5
8	100	-10	1,000	10	15
9	100	10	1,000	10	20

Table 3

Sample No.	Upper-layer coating film			Total thickness of upper- and lower-layer coating films (µm)
	Acrylic resin		Thickness (µm)	
	Acid value	Glass transition temperature (°C)		
Example				
1	100	40	3	8
2	100	40	0.5	1
3	100	80	3	5
4	200	45	1	5
5	300	60	2	10
6	300	50	5	15
7	40	40	2	8
8	40	40	10	20
Comparative Example				
1	100	40	10	20
2	100	30	0.2	0.4
3	100	40	5	15
4	35	30	10	15
5	100	80	4	10
6	400	40	2	7
7	100	85	10	15
8	100	40	5	20
9	100	40	5	25

Table 4

Sample No.	Coating film solubility	Coating film adhesion	Dragging resistance	Blocking resistance
Example				
1	AA	AA	A	AA
2	AA	AA	AA	AA
3	A	AA	AA	AA
4	AA	AA	AA	AA
5	A	AA	A	AA
6	AA	AA	A	AA
7	A	AA	A	A
8	A	AA	A	AA
Comparative Example				
1	AA	A	B	AA
2	C	AA	B	C
3	C	A	B	AA
4	C	A	B	B
5	A	A	B	AA
6	AA	AA	B	AA
7	Evaluation was impossible because of cracks produced in coating films.			
8	AA	AA	B	A
9	AA	AA	B	AA

<u>Example 2</u>

Methyl methacrylate, butyl acrylate and methacrylic acid were copolymerized to synthesize an acrylic resin having an acid value of 100 and a glass transition temperature of 10°C. This acrylic resin was allowed to react with an epoxy oligomer having a molecular weight of 1,000 to obtain an epoxy-modified acrylic resin modified to a degree of 10% by mass. Then, a treating emulsion of this resin was coated on the surfaces of the same stainless steel sheets as used in Example 1 by means of a bar coater, followed by drying in an oven to form on each steel sheet a lower-layer coating film with a layer thickness of 5 µm. Thereafter, methyl methacrylate, butyl acrylate and methacrylic acid were copolymerized to synthesize an acrylic resin having an acid value of 100 and a glass transition temperature of 40°C. To the treating emulsions obtained, polyethylene resin powder and/or fluorine resin powder was/were added, and the mixtures obtained were left to stand in an atmosphere of 40°C for 10 days or 20 days. After leaving, the treating emulsions obtained were each coated on the lower-layer coating film in the same manner as the above, followed by drying to form each upper-layer coating film. Table 5 shows the treating emulsions used for the upper-layer coating film and also shows the results of the following tests made on the acrylic-resin coating-film coated stainless steel sheets thus obtained.

(1) Treating emulsion stability:

The acrylic resin treating emulsions for the upper-layer coating film were hermetically enclosed in glass containers, and those which neither thickened nor gelled even when left to stand in an atmosphere of 40°C for 20 days were evaluated as "AA"; those which neither thickened nor gelled during the first 10 days, as "A"; those which thickened or gelled before the lapse of 10 days, as "C".

(2) Workability:

Using disk test pieces, cylinder drawing was tested (punch diameter: 40 mm; draw ratio: 2.35; blank holding force: 2.5×10^4 N). Regarding test piece diameter before working as L_1 and test piece average diameter after working as L_2, those in which L_2/L_1 was less than 0.88 were evaluated as "AA"; from 0.88 to less than 0.90, as "A"; from 0.90 to less than 0.94, as "B"; and 0.94 or more, as "C".

(3) Resistance to dragging:

Evaluated in the same manner as in Example 1.

Table 5

Sample No.	Upper-layer coating film				Upper/ lower layers total thickness (µm)	Emulsion stability	Workability	Dragging resistance
	Resin powder							
	Type	Amount (mass%)	Average particle diam. (µm)	Thickness (µm)				
11	I	5	0.1	2	7	AA	A	AA
12	II	10	0.5	3	8	AA	A	AA
13	III	1	2	7	12	AA	AA	AA
14	III	2	4	10	15	AA	AA	AA
15	III	5	1	3	8	AA	AA	AA
16	III	10	1.5	5	10	AA	AA	AA
17	III	25	10	15	20	A	AA	AA
11	I	30	1	(*2)	-	C	-	-
12	II	10	0.01	2	7	AA	B	A
13	III	10	0.05	3	8	AA	B	A
14	III	25	13	3	8	A	B	A
15	III	0.5	1	5	10	AA	B	A
16	III	30	4	(*2)	-	C	-	-
17	-	0	-	5	10	AA	B	A

Remarks:
(1) In the item of "Resin powder", I: polyethylene resin powder; II: fluorine resin powder; and III: a 9/1 (weight ratio) mixture of polyethylene resin powder and fluorine resin powder.
(2) *2: Treating emulsions of Comparative Samples 11 and 16 gelled and were difficult to coat.

Claims

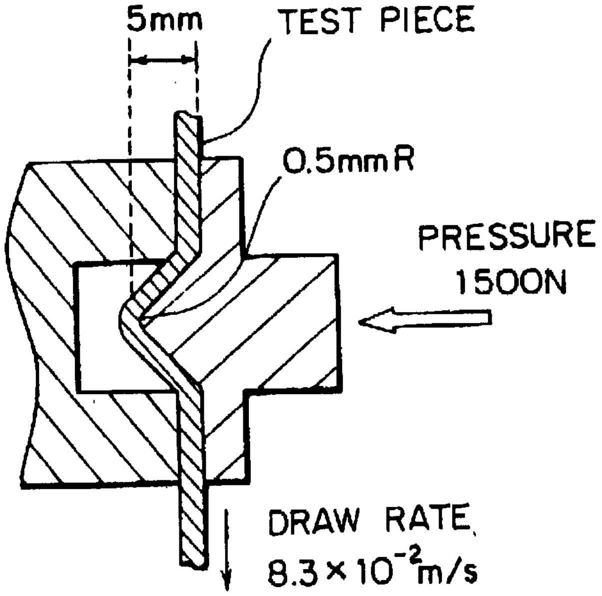
1. An alkali-soluble protective-film coated stainless steel sheet comprising a stainless steel sheet and successively formed on its surface i) a lower-layer coating film formed of an epoxy-modified acrylic resin obtained by modifying an acrylic resin having an acid value of from 40 to 300 and a glass transition temperature of from 0°C to 20°C with an epoxy oligomer having a molecular weight of from 500 to 2,000, to a degree of from 3% by mass to 20% by mass, and ii) an upper-layer coating film formed of an acrylic resin having an acid value of from 40 to 300 and a

glass transition temperature of from 40°C to 80°C; the upper- and lower-layer coating films having a total thickness of from 1 μm to 20 μm.

2. The alkali-soluble protective-film coated stainless steel sheet according to claim 1, wherein said acrylic resin for the lower-layer coating film and the upper-layer coating film is a polymer of acrylic acid and/or methacrylic acid, or a copolymer of at least one of these monomers with an acrylate and/or a methacrylate.

3. The alkali-soluble protective-film coated stainless steel sheet according to claim 1, wherein said upper-layer coating film on the stainless steel sheet contains from 1% by mass to 25% by mass of a high-polymer resin powder having an average particle diameter of from 0.1 μm to 10 μm.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/02533

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 B32B15/08, B05D7/14

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)

Int. Cl^6 B32B15/08, B05D7/14

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

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 56-44768, A (Dai Nippon Toryo Co., Ltd.), April 24, 1981 (24. 04. 81)(Family: none)	1 - 3
E	JP, 8-252887, A (Nisshin Steel Co., Ltd., Dainippon Ink and Chemicals, Inc.), October 1, 1996 (01. 10. 96)(Family: none)	1 - 3

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

* Special categories of cited documents:
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