

[54] SEMI-FERRITIC STAINLESS MANGANESE
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[63] Continuation of Ser. No. 42,037, June 1, 1970,
abandoned.

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[52] U.S. Cl. 148/12 EA; 148/37; 148/135

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[58] Field of Search 75/123; 148/136, 135

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[57]

ABSTRACT

A semi-ferritic stainless steel having a austenite content while hot of from 10 to 50%, and a composition of 0.2% max. C, 1 – 10% Mn, 3% max. Si, 5% max. Ni, 14 – 25% Cr, 3% max. Mo, 5% max. Cu, 0.3% max. N₂, 10% max. Co, 1% max. Ti, 1.0% max. Cb, 0.005% max. B, 0.5% max. Al, the balance Fe and incidental impurities. The composition is characterized by particular nickel and chromium equivalents. The steels are treated to retain the austenite and ferrite at ambient temperatures, and then the austenite is transformed into martensite and subsequently the martensite is transformed into ferrite and carbides.

11 Claims, 1 Drawing Figure

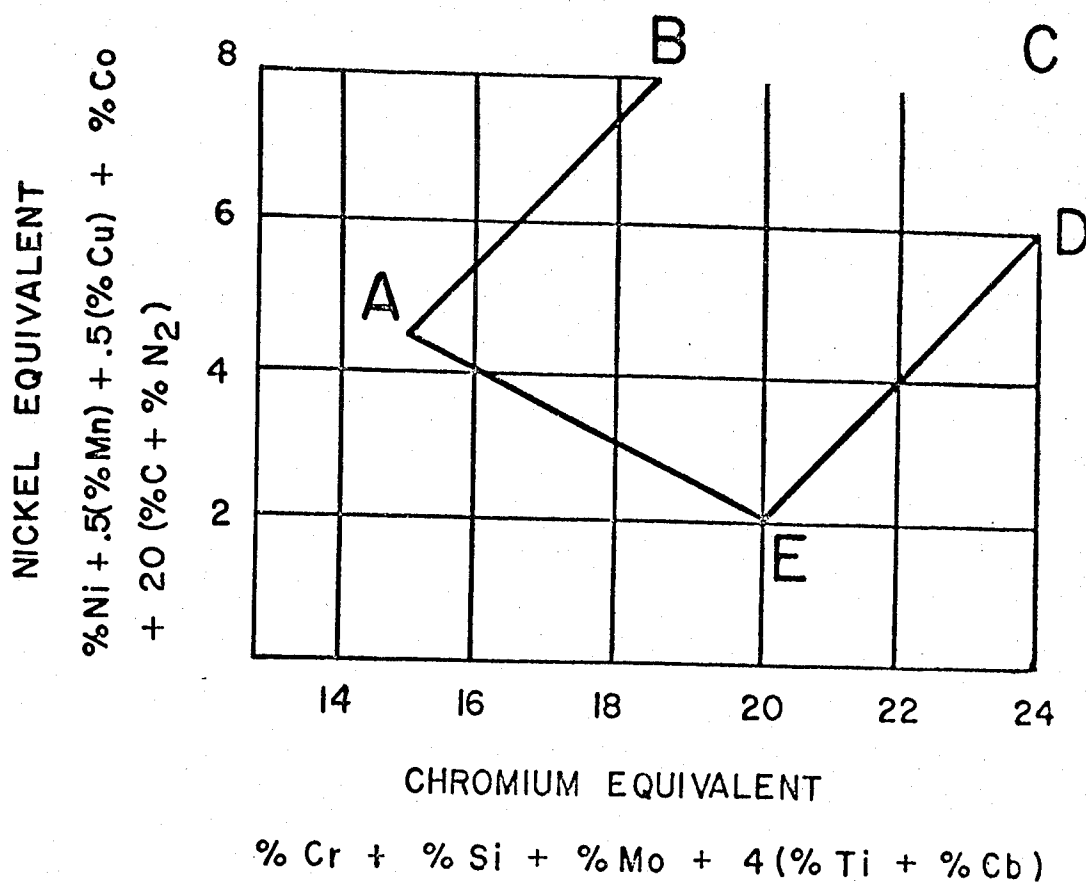


Fig. 1

SEMI-FERRITIC STAINLESS MANGANESE STEEL

This is a continuation of application Ser. No. 42,037, filed June 1, 1970, now abandoned.

Our invention relates to stainless steels and, more particularly, to semi-ferritic stainless steels and methods of treating them.

A variety of different stainless steel types are known, each having its particular characteristics. These general types are presented in Table I, along with typical chemical compositions for various designations within the general type.

TABLE I

Type	Desig.	C	Mn	Stainless Steels Chemical Analysis (Weight Percent)				Cr	Mo	Ti	Cb	Cu
				Si	P	S	Ni					
Semi-Ferritic	AFNOR Z 8 C 17	.1 max.	1. max.	1. max.	.04 max.	.03 max.	≤ .5	16-18				
	Z 8 CD 17	.1 max.	1. max.	1. max.	.04 max.	.03 max.	≤ .5	16-18	.9/1.3			
	Z 10 CF 17	.12 max.	1.5 max.	1. max.	.06 max.	≥ .15	≤ .5	16-18				
Semi-Ferritic	Werkstoff No. 4510	.1 max.	1. max.	1. max.				17		>7(C)		
Ferritic	Werkstoff No. 4511	.1 max.	1. max.	1.5 max.				17.5			>12(C)	
Austenitic	AFNOR Z 10 CN 18-09	.12 max.	2.0 max.	1.0 max.	.04 max.	.03 max.	8-10	17-19				
Austenitic	AFNOR Z 6 CND 17-11	.07 max.	2.0 max.	1.0 max.	.04 max.	.03 max.	10-12	16-18	2.0-2.5			
Austenitic	AISO 2 01	.15 max.	5.5-7.5	1.0 max.	.06 max.	.03 max.	3.5-5.5	16-18				
Austeno-Ferritic	Typical	.05	10	.5			2.0	18			.4	
Austeno-Ferritic	Typical	.05	.5	.5			8	20	2.5			1.5
Austeno-Ferritic	Typical	.05	.5	.5			6.5	26		.2		

The semi-ferritic stainless steels are characterized by a mixed structure of delta ferrite and austenite when hot, the austenite transforming to martensite on cooling, and the martensite transforming to alpha ferrite and carbides after tempering. The transformation from austenite to martensite takes place by rapid cooling to below the critical temperature (A₁) of about 850°C and transformation of martensite to alpha-ferrite takes place by tempering below the A₁. The final structure of alpha and delta ferrite and carbides is the traditional structure employed for applications of rods, sheets and wires, into which the semi-ferritic steels are easily transformed.

However, the rapid cooling of semi-ferritic steels while hot causes grain enlargement of the delta ferrite, as well as the transformation of the austenite into martensite. This is particularly troublesome in weld areas where a fragile martensitic phase forms about the ferritic grains. Further, the semi-ferritic steels, which are reactant to corrosion under tension in chloride solution, have other corrosion resistance inadequacies.

Attempts to improve the weldability problems economically have been tried by using compositions which result in a complete ferritic structure. This is accomplished by adding titanium or columbium as shown for the Werkstoff alloys in Table I. However, a complete ferritic structure is very prone to grain growth, and further, processing problems while hot are acute because of the inherent softness of the ferritic structure.

These 17% chromium steels can be transformed entirely into an austenitic structure by adding nickel, manganese or a suitable combination of the two. These

steels, which are also shown in Table I, are generally used in a full hardened state or cold-worked state, or sometimes after an appropriate low temperature stress relief.

These austenitic steels have the advantage of good weldability and satisfactory resistance to corrosion, but the disadvantage of involving a marked increase in the cost of the alloy due to the addition of nickel or a combination of the elements nickel and molybdenum, of exhibiting a special susceptibility to corrosion under tension which limits their use for certain applications (water heating), and of having a low elastic limit.

The so-called austeno-ferritic steels form an intermediate group between semi-ferritic and austenitic steels. Their analysis, as given in Table I, is so selected as to produce a biphased structure, i.e., austenite + ferrite. The fundamental difference between this family of steels and semi-ferritic steels, which also contain a relatively substantial quantity of austenite while hot, is due to the special stability of this biphasic structure compared to semi-ferritic steels whose structure after tempering is decomposed into ferrite + carbide, as shown above.

The standard thermal treatment for the austeno-ferritic steels before use, is a heat treatment around 1050°-1150°C.

These austeno-ferritic steels present the advantage of having an improved weldability compared with semi-ferritic steels whose tendency is the enlargement of the grain, and further, they provide an improvement as far as resistance to corrosion under tension is concerned as compared to austenitic steels. The disadvantage of the austeno-ferritic steels is the difficulty in processing when hot, and in addition, due to the composition, a significant increase in the price is necessary.

Our invention provides a semi-ferritic steel in which the fragile martensite phase is not formed and, therefore, the weldability is greatly improved. Further, the corrosion resistance is substantially improved over semi-ferritic steels known heretofore.

The composition limits are such that the alloy can be economically produced and because of certain critical heat treatments, can be economically processed. In fact, a substantial gain in productivity in the manufac-

ture of sheets, rods and wires is obtained because of the notable reduction in the total time that heat treating furnaces are used.

The steels of the invention have a austenite content while hot of from 10 to 50% by weight, and a composition comprising by weight 0.2% max. C, 1 - 10% Mn, 3% max. Si, 5% max. Ni, 14 - 25% Cr, 3% max. Mo, 5% max. Cu, 0.3% max. N₂, 10% max. Co, 1% max. Ti, 1.0% max. Cb, 0.005% max. B, 0.5% max. Al, and the balance Fe and incidental impurities. The composition is also characterized by the fact that it has representative points in a system of coordinates (equivalent Cr — equivalent Ni) which are included in the interior of a pentagon which has the following points as its corners, A (15, 4.5), B (18.5, 8), C (24, 8), D (24, 6) and E (20, 2). While hot, these steels have a structure identical to that of semi-ferritic steels (ferrite + austenite), but they preserve this biphasic structure when cooled without the formation of a fragile martensitic phase. In other words, this austenite is retained and is later transformed to martensite and subsequently to ferrite and carbides by treatments which form a part of this invention.

FIG. 1 is a graph showing the composition limits of our invention in terms of nickel and chromium equivalents.

The broad composition limits of our invention and three preferred ranges (shown as A, B and C) within the broad range, are set forth in Table II.

TABLE II

	Analysis of Stainless Steels (% By Weight)			
	Broad	Preferred A	Preferred B	Preferred C
C	.2 max.	.1 max.	.1 max.	.1 max.
Mn	1 - 10	3 - 6	3 - 6	3 - 6
Si	3 max.	1 max.	1 max.	1 - 2
Ni	5 max.	1 max.	1 max.	1 max.
Cr	14 - 25	18 - 22	15 - 18	15 - 18
Mo	3 max.	1.5 max.	1.5 - 3.0	.5 - 2.0
Cu	5 max.	1 max.	1 max.	1 max.
N ₂	.3 max.	.1 max.	.1 max.	.1 max.
Fe	Balance	Balance	Balance	Balance
Co	10 max.			
Ti	1 max.			
Cb	1.0 max.			
B	.005 max.			
Al	.5 max.			

The "Preferred A" composition is economically advantageous because of the limited amounts of expensive additive elements. The "Preferred B" composition, in addition to economy, exhibits outstanding resistance to corrosion. "Preferred C" composition is similar to "Preferred B" composition in properties and differs only in that a portion of the molybdenum is replaced by silicon. When it is desired to improve the machinability of the steels of the invention, one may add to them in

The various analyses are further limited by their chromium and nickel equivalents. For the chromium equivalent we use (% Cr) + (% Si) + (% Mo) + 4 (% Ti + % Nb). For the nickel equivalent we use (% Ni) + 0.5 (% Mn) + 0.5 (% Cu) + (% Co) + 20 (% C + % N₂). As shown in FIG. 1, the limitation in terms of the chromium and nickel equivalents is represented by a pentagon in which the chromium equivalent is the abscissa and the nickel equivalent is the ordinate and the pentagon can then be defined by the following ordinates, A (15, 4.5), B (18.5, 8), C (24, 8), D (24, 6) and E (20, 2).

The steels of the invention which are delivered in the form of sheets, rods, or wires receive the usual manufacturing operations of semi-ferritic steel of the Z 8 C 17 type, namely blooming, hot rolling, heat treating and cleaning, cold rolling or wire drawing, and final heat treating. The heat treatment which follows the final pass of hot rolling is normally a prolonged annealing at a temperature on the order of 800°C which leads to the maximum softening favorable to the subsequent operations of deformation while cold.

According to the new method of carrying out this heat treatment which forms part of the invention, one operates in two stages, the first being a transformation into martensite of the austenite retained at ambient temperature, and the second being a transformation of this martensite into ferrite and carbides. This latter stage is referred to as tempering, i.e., the conversion of martensite to ferrite and cementite after the steel has been hardened by the prior heat treatment.

The first stage can be accomplished by any of the following four alternatives:

1. Annealing between 700° and 900°C, preferably between 750 and 800°C, for instance for about 4 hours, followed by a slow cooling on the order of 25°C per hour down to 650°C, then cooling in the air;
2. Cryogenic treatment, for instance 3 hours at -80°C;
3. Cold reducing at ambient temperature, for instance rolling or wire drawing while cold with reduction of the section of at least 30%;
4. Slow cooling from the exit temperature from the last hot roll pass (for instance cooling of 25°C/hr. from 850°C to 650°C) then cooling in the air.

The second stage is tempering at a temperature lower than 850°C that is continued until the martensite disappears. Its duration, which may be an hour or even less, is substantially reduced compared to that of the usual single annealing of 10 to 20 hours, and this improves the profitability of the treating furnaces.

By way of example 5 heats of steel according to the invention were made. Their analyses appear in the following Table III.

TABLE III

Heats	Experimental Heats Composition (Weight Per Cent)								
	C	Si	Mn	Ni	Cr	Mo	S	P	N ₂
(1)	0.058	0.4	4.7	0.5	20.0	0.02	0.005	0.019	0.051
(2)	0.063	0.4	9.2	0.2	23.1	0.01	0.005	0.019	0.052
(3)	0.044	0.3	4.4	0.1	17.4	1.98	0.016	0.023	0.024
(4)	0.045	1.3	7.6	0.8	17.1	0.98	0.014	0.023	0.023
(5)	0.064	1.9	5.2	0.1	16.8	0.96	0.017	0.025	0.050

known manner sulfur and/or selenium, and/or tellurium in amounts not exceeding 0.4%, in all.

Their mechanical characteristics were determined after treatment in accordance with our invention. Cy-

lindrical test pieces 10 mm in diameter, obtained by forging, were subjected to an annealing at 785°C for 4 hours followed by cooling of 25°C per hour to 650°C and then air cooling; thereupon tempering at 750°C for 15 minutes following with air cooling. The results appear in the following Table IV.

TABLE IV

Casting	Test Results of Experimental Heats			
	R (h bar)	E (h bar)	A % ($L_{0.2} = 50$ mm)	E%
(1)	56	33	30	56
(2)	58	34	29	58
(3)	59	35	26	58
(4)	63	39	25	58
(5)	68	44	31	77

The bending characteristics, as evidenced by bend tests, in the absence of any thermal treatment, of the welds of the steels of the invention is definitely superior to that of the usual semi-ferritic steels. The comparison of the micro-hardness of the different components encountered in the welding of conventional semi-ferritic steels and steels of our invention led to the results shown in the following Table V.

TABLE V

	Micro-Hardness Results	
	Vickers Micro-Hardness (Load Applied 50 g)	
	inside the ferritic grains	at the joints of the ferritic grams
Conventional semi-ferritic steel	220	530 (Martensitic phase)
Steel of the invention	260	320 (Austenitic phase)

The poor resilience of the fusion weld is characteristic of semi-ferritic stainless steels. This resilience is greatly increased in the steel of the invention as shown by Table VI below:

TABLE VI

Steels	Weld Resilience	
	Resilience: Charpy V in dal/cm ²	
Semi-ferritic (Z 8 C 17)	< 0.5	
Ferritics (Werkstoff 4510 and 4511)	0.5 to 1.5	
Austeno-ferritics	1.5 to 3	
Austenitics (AISI 201 and 202)	> 4	
Steels of the invention	2 to 4	

From the point of view of corrosion, the two principal modes to which stainless steels can be subjected in practice are corrosion by pitting in the presence of Cl⁻ ions and general corrosion in a diluted acid and unchlorinated medium. The following tests were made on sheets of 10 mm thickness. The steels of our invention, after hot rolling, were subjected to treatment also in accordance with our invention.

1. Corrosion by pitting in the presence of Cl⁻ ions in a solution that was non-oxidizing in itself, but aerated. This type of corrosion simulates certain atmospheric corrosion (Cl⁻ ions always present, even far from the sea) and corrosion of saline solutions, e.g., food products, etc. These very chlorinated or freely oxidizing solutions often warrant steels having at least 10 - 18 Mo.

The resistance to corrosion in this field has been estimated by the potential for pitting in sodium chloride solutions by means of an anodic polarization curve. It has been shown, in fact, that the cathodic reaction of oxygen reduction was insensitive to the gradation, and the determination of the potential for pitting (anodic characteristic) therefore constitutes a good scale for classifying the gradations.

In the form of intervals the following Table VII gives the results of comparative tests on the various steels indicated.

TABLE VII

	Potential for Pitting	Potential of Pitting (in a V) in a Na Cl, 0.02 M Medium
Semi-ferritic steels (Z 8 C 17)		530-580
Ferritic Steels (Werkstoff 4510 and 4511)		540-590
Austeno-ferritic steels		650-730
Austenitic manganese steels (AISI 201 and 202)		610-660
Austenitic nickel steels (Z 10 CN 18 - 09)		640-700
Steels of the invention		620-680

2. General corrosion in a diluted and non-chlorinated acid medium. In the great majority of cases, a stainless steel should be found in the passive state to resist corrosion in an acid medium, otherwise it will be corroded in the active state.

In a given acid solution a given stainless steel will be passive if the cathodic reaction of reduction of the oxidizer in solution (dissolved oxygen, ions Fe³⁺, Cu²⁺, etc.) brings the potential of the metal into the zone of passivity. This will be the case if the speed of reduction of the oxidizer, expressed in A/cm², is greater than the critical intensity of passivation i_c per cm² measured on the anodic polarization curve of the metal traced in the absence of an oxidizer. Inversely, for a given speed of reduction of the oxidizer the steels will be passive that have an i_c smaller than this speed, and the steels will be active that have an i_c that is greater. Accumulated experience has shown that at least in a very large area it is indeed i_c which is the deciding parameter. The smaller the i_c is, the "better" the steel will be. The results of the tests in this area are presented in Table VIII.

TABLE VIII

Steels	Corrosion Passivation Critical Course of Passivation (10 ⁻³ A. cm ⁻²) in an H ₂ SO ₄ 2 M Medium
Semi-ferritic (Z 8 C 17)	11 - 15
Ferritic (Werkstoff 4510-4511)	10 - 15
Austeno-ferritic	0.5 - 4
Manganese austenitic (AISI 201-202)	5 - 9
Nickel austenitic (Z 10 CN 18-09)	0.7 - 1.5
Steels of the invention	2 - 6

In a general manner, the preceding results make it possible to locate the alloys of our invention at a level that is intermediate between austenitic nickel steels and traditional semi-ferritic steels.

The applications of the steels of the invention in the form of rods, sheets, and wires are very varied. Besides

the usual usage of semi-ferritic steels, austenitic manganese or low content nickel steels, such as the copper-smith's trade, architecture, sinks, hubcaps, bumpers, moulding for automobile decoration, they have new markets due to their price which is lower than that of austenitic steels and austenoferritic steels and also due to the improved quality that they present compared to semi-ferritic steels. Moreover, they are particularly suitable for the manufacture of hot water flasks, automobile radiators (because of their resistance to corrosion under tension, their weldability and their price), mufflers, welded pipes, stove grills (because of their weldability), hooks for attaching the slate for roofs (because of their resistance to corrosion).

We claim:

1. A process for treating a semi-ferritic stainless steel having an in-use structure of alpha and delta ferrite and carbides, characterized by high strength properties, good bending characteristics, good micro-hardness, good fusion weld resilience and good corrosion resistance, both in the presence and absence of chlorine and acid media, comprising:

A. Preparing a steel having a composition selected from the group consisting of by weight 0.1% max. C, 3-6% Mn, 1% max. Si, 1% max. Ni, 18-22% Cr, 1.5% max. Mo, 1% max. Cu, 0.1% max. N₂ and the balance Fe and incidental impurities, 0.1% max. C, 3-6% Mn, 1% max. Si, 1% max. Ni, 15-18% Cr, 1.5-3.0% Mo, 1% max. Cu, 0.1% max. N₂ and the balance Fe and other incidental impurities and 0.1% max. C, 3-6% Mn, 1-2% Si, 1% max. Ni, 15-18% Cr, 0.5-2.0% Mo, 1% max. Cu, 0.1% max. N₂ and the balance Fe and other incidental impurities, said steel characterized by chromium and nickel equivalents falling within the pentagon on the graph of the sole FIGURE, said pentagon having as its ordinates, A (15, 4.5) B (18.5, 8), C (24, 8), D (24, 6), E (20, 2);

B. Hot working said steel so as to maintain an austenite content while hot of from 10 to 50%, the balance being delta ferrite;

C. Cooling said steel to retain said austenite at room temperature;

D. Treating said steel to transform the austenite into martensite; and

E. Tempering the martensite to transform the martensite into alpha ferrite and carbides.

2. A process for treating a semi-ferritic stainless steel having an in-use structure of alpha and delta ferrite and carbides, characterized by high strength properties, good bending characteristics, good micro-hardness, good fusion weld resilience and good corrosion resistance,

both in the presence and absence of chlorine and acid media, comprising:

A. Preparing a steel having a composition selected from the group consisting of by weight 0.1% max. C, 3-6% Mn, 1% max. Si, 1% max. Ni, 18-22% Cr, 1.5% max. Mo, 1% max. Cu, 0.1% max. N₂ and the balance Fe and incidental impurities, 0.1% max. C, 3-6% Mn, 1% max. Si, 1% max. Ni, 15-18% Cr, 1.5-3.0% Mo, 1% max. Cu, 0.1% max. N₂ and the balance Fe and other incidental impurities and 0.1% max. C, 3-6% Mn, 1-2% Si, 1% max. Ni, 15-18% Cr, 0.5-2.0% Mo, 1% max. Cu, 0.1% max. N₂ and the balance Fe and other incidental impurities, said steel characterized by chromium and nickel equivalents falling within the pentagon on the graph of the sole FIGURE, said pentagon having as its ordinates, A (15, 4.5), B (18.5, 8), C (24, 8), D (24, 6), E (20, 2);

B. Hot working said steel so as to maintain an austenite content while hot of from 10 to 50%, the balance being delta ferrite;

C. Annealing the steel for a prolonged period at about 800°C so as to transform the austenite to alpha ferrite and carbides; and

D. Cold forming the steel.

3. The process of claim 1 wherein the treating of step D includes annealing between 700° and 900°C for about 4 hours, slow cooling at a rate of about 25°C per hour down to 650°C, and then air cooling.

4. The process of claim 1 wherein the treating of step D includes cryogenically treating at about -80°C for about 3 hours.

5. The process of claim 1 wherein the treating of step D includes cold working at ambient temperature by a cold reduction of at least 30%.

6. The process of claim 1 wherein the treating of step D includes slow cooling from a last processing hot rolling pass at a rate of about 25°C per hour to 650°C and then air cooling.

7. The process of claim 1 wherein the tempering of step E includes annealing at a temperature less than 850°C until the martensite disappears.

8. The process of claim 1 wherein the annealing is between 750° and 800°C.

9. The process of claim 1 wherein the annealing is for a duration of less than 1 hour.

10. The product made in accordance with the process of claim 1.

11. The product made in accordance with the process of claim 10.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,926,685
DATED : December 16, 1975
INVENTOR(S) : Andre Gueussier et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Page 1 of the Patent - After the line listing the inventors insert:

--Assignee: Ugine Aciers - Paris, France--.

In Table I - Under the heading entitled Desig. "AISO" should read --AISI--.

Column 4 Line 37 "25+C" should read --25°C--.

Claim 1 - Column 7 Line 27 "mac. C," should read --max. C, --.

Claim 2 - Column 8 Line 6 ".01%" should read --.1%--.

Claim 11 - Column 8 Line 51 "10" should read --2--.

Signed and Sealed this

Twenty-ninth Day of November 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks