

[54] **REFRACTORY IRON-BASE ALLOY
RESISTING TO HIGH TEMPERATURES**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 78,608, Oct. 6,
1970, abandoned.

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[58] Field of Search **75/122, 128, 171, 134 F;**
148/31, 32

[56] **References Cited**

UNITED STATES PATENTS

2,553,330 5/1951 Post **75/122 X**

2,570,193 10/1951 Bieber et al. **75/171 C**
3,495,977 2/1970 Denhard et al. **75/171 X**
3,512,963 5/1970 Schramm **75/170**
3,516,826 6/1970 Ward et al. **75/171**
3,552,950 1/1971 Rundell et al. **75/122**

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[57] **ABSTRACT**

The refractory iron-base alloy according to the inven-
tion has the following composition:

	Percent by weight
Carbon	from 0.05 to 0.20
Nickel	from 30 to 40
Chromium	from 20 to 30
Columbium	from 0.2 to 2
Nitrogen	from 0.04 to 0.2
Manganese	from 0.6 to 2
Silicon	from 0.8 to 2
Iron and impurities	complementary percentage

Said alloy offers high resistance to creep, thermal
shocks, heat fatigue and intergranular oxidation, as
well as good weldability.

More specifically, the proportion of the various
elements comply with the formula:

$$30 \times C \% + Ni \% + 0.5 \times Mn \% + 16 \times N \% = Cr \% \\ + 0.5 \times (Nb + \frac{1}{2} Ta) \% + 3.5 \times Ti \% + 1.5 \times Si \% + \\ Mo \% + 11 \pm 2.$$

7 Claims, No Drawings

REFRACTORY IRON-BASE ALLOY RESISTING TO HIGH TEMPERATURES

The present invention is a Continuation-in-Part of our United States patent application Ser. No. 78,608 filed Oct. 6, 1970, now abandoned.

The present invention has for its object a refractory ironbase alloy possessing simultaneously a set of highly satisfactory properties at high temperatures comprised between 600°C and 1,250°C, owing to which the said alloy is particularly suitable for the manufacture of parts adapted to work at high temperatures, for instance outside or inside reforming and/or cracking furnaces, under particularly severe operating conditions.

The present invention also concerns all articles or elements constituted by the said refractory alloy.

The parts working outside reforming or cracking furnaces are subjected to high temperatures, considerable temperature gradients and abrupt coolings, so that the alloys known at present, the characteristics of which are not sufficiently adapted for such use, do not afford sufficiently long working life and limit the performance of the said furnaces.

The refractory alloys usually employed for such purposes are either refractory alloys in the rolled or laminated state, comprising for instance at least 0.08 % of carbon, about 32 % of nickel and about 21 % of chromium, or moulded refractory alloys containing for instance about 0.4 % of carbon, about 20 % of nickel and about 25 % of chromium, the carbon content of the said alloys being generally superior to about 0.20 %.

All the above-mentioned percentages as well as the percentages given in the following description are percentages by weight.

The working conditions of the parts or the form of the assemblies composed thereof limits the use of the known alloys of the aforesaid type, in the welded state; moreover, the creep resistance of these alloys is generally insufficient. In the particular case of more than 0.20 %-carbon moulded alloys, which are very sensitive to thermal variations, there very frequently occur premature breakages of the parts made from such alloys.

The alloy according to the present invention remedies all the aforesaid drawbacks and may be used to make parts capable of constituting assemblies of quite various forms and of being used under very severe conditions such as those mentioned above in the case of the outside of reforming and/or cracking furnaces.

Thus, in a particular embodiment of the invention, the composition of said alloy is more particularly adapted to constitute metallic parts to be used on the outside of a reforming and/or cracking furnace.

In another particular embodiment of the alloy according to the invention, said alloy is intended to be used inside the reforming and/or cracking furnaces wherein there exists an oxidizing and flame atmosphere and a temperature which may reach 1,250°C, on the metallic parts used inside the furnace, instead of about 1,100°-1,150°C on the metallic parts used outside the furnace, the temperature of the inside metallic parts being however more stable than the temperature of the outer metallic parts.

The refractory alloy according to the present invention possesses simultaneously the following properties:

high creep resistance up to 1,250°C,
high resistance to inter-granular oxidation even at high temperatures in oxidizing atmospheres,
a very good general resistance to oxidation up to 1,250°C for certain specific compositions, the said resistance being however quite satisfactory up to 1,150°C,

high resistance to thermal shocks, due mainly to sufficient ductility and holding in course of time at working temperatures, enabling this alloy to be deformed locally when the said thermal shocks occur,

good resistance to heat stress or fatigue,

good weldability during the carrying out of any known industrial welding processes,

good aptitude to deformability in the hot state, enabling shaping by way of bending without by any means worsening the weldability properties or the other properties mentioned hereabove.

The forgeability of the alloy according to the invention enables to carry out hot shaping of rough castings and to make for instance from the latter forged, laminated or rolled parts or elements. The preservation of the main mechanical properties subsequent to hot shaping as well as the preservation of the weldability properties enable to construct satisfactory assemblies with elements proceeding from one and the same manufacturing process.

Said alloys are characterized by the following composition:

C	0.05	-	0.20	%	by weight
Ni	30	-	40	%	do.
Cr	20	-	30	%	do.
Nb	0.2	-	2	%	do.
N	0.04	-	0.2	%	do.
Mn	0.6	-	2	%	do.
Si	0.6	-	2	%	do.
Ta	0	-	0.3	%	do.
Ti	0	-	1	%	do.
Mo	0	-	0.5	%	do.
Al	0	-	0.05	%	do.
Pb	0	-	0.01	%	do.
Sn	0	-	0.01	%	do.
Zn	0	-	0.01	%	do.
Cu	0	-	0.25	%	do.
Other impurities	0	-	0.50	%	do.
Fe	complementary percentage				

According to the preferred form of embodiment of the present invention, the respective proportions of the various elements comply with a basic formula resulting in the improvement of at least some of the following properties: creep resistance, resistance to thermal shocks, resistance to corrosion at high temperatures by oxygen, carbon, sulphur or any other corrosive element likely to come into contact with the alloy, more particularly resistance to intergranular oxidation, weldability, resistance to ageing, more particularly thermal ageing, good aptitude to deformation in the hot state enabling the said alloy to be readily shaped by way of bending, forging, etc.; such properties allow the alloy to resist at best to the contact of the combustion gases, which always have an oxidizing effect owing to the excess of air required for the combustion of the fuel used as a heating means for the said furnaces.

The aforesaid basic formula is as follows:

$$30 \times C \% + Ni \% + 0.5 \times Mn \% + 16 \times N \% = Cr \% + 0.5 \times (Nb + \frac{1}{2} Ta) \% + 3.5 \times Ti \% + 1.5 \times Si \% + Mo \% + 11 \pm 2$$

wherein C %, Ni %, Mn %, N %, Cr %, Nb %, Ta %, Ti

%, Si % and Mo % represent respectively the ponderal percentage of each cited element.

Where the respective proportions of the various elements comply with the aforesaid general composition and also with said formula, suitable relative proportions for the austenitic and ferritic phases are maintained. In the said formula, the elements mentioned on the left-hand side are austenizing or gamma-producing elements, whereas the elements in the second member are ferritizing or alpha-producing elements; in the case of titanium and of molybdenum, the contents of Ti, Ta and Mo may be zero as indicated above.

Preferably, one manages to have the following formula complied with: $A = B \pm 20\%$ with $A = 30 \times C\%$

$$B = 2 \times \text{Ti \%} + 6 \times (\text{Nb} + \frac{1}{2} \text{Ta}) \%$$

By complying with the above-mentioned two formulas, maximum stabilization of the austenetic and ferritic phases is obtained and intergranular corrosion through oxidation at high temperatures, on the order of from 900° to 1,250°C, is thus completely avoided.

According to one feature of the present invention, it is highly preferable, more particularly for alloys used for constituting metallic parts inside reforming and/or cracking furnaces, that the silicon proportion be comprised between 1.0 and 1.8 % by weight; indeed, where the proportion is less than 1.0 %, resistance to oxidation and recarburization is insufficient above 1,150°C and it does not become excellent unless the said proportion is at least on the order of 1.2 %; where the silicon proportion is higher than 1.8 % weldability is poor and it is preferable that this proportion be at most equal to 1.5 % in order that weldability and ductility be excellent; the chromium proportion should be comprised preferably between 23 and 30 %, and more advantageously between 24 and 28 % in order to obtain the best resistance to oxidation and corrosion without prejudice to the other properties; the nickel proportion is then preferably higher than 33 % to increase the maximal temperature of use.

Preferably, the proportion of titanium should be approximately twice that of the carbon proportion, whereas the niobium proportion (in the absence of tantalum) should be at least equal to six times the carbon proportion in order to maintain adequate creep resistance irrespective of the carbon proportion within the said range (0.05–0.20 %).

Niobium may be partially replaced by tantalum, as appears from the preceding formulas corresponding to the conditions of maximum stabilization, the proportions in this case being two parts of tantalum for one part of niobium; it will be noted that tantalum is generally present, owing to the fact that the niobium of usual grade used generally to form niobium alloys contains a certain proportion of tantalum as an impurity.

Molybdenum is an unarmful impurity provided the proportion thereof does not exceed 0.50 %.

The Applicant has also discovered that certain elements frequently encountered among the impurities in iron, in addition to phosphorous and sulphur, the sum of which should be preferably limited to 0.05 %, are particularly harmful to some of the desired properties of the alloy of the invention; for this reason, the proportions of casual impurities such as aluminium, lead, tin, zinc and copper are limited respectively to 0.05 %-0.01 %-0.01 % - 0.01 % and 0.25 %. The effect of these ele-

ments is either to reduce cold or hot ductility, or to render hot forming more difficult or, again, to reduce creep resistance or thermal fatigue.

Ordinary microscope and electronic microscope examination of raw cast samples of the alloys of the present invention reveals an austenitic structure in which are finely dispersed carbide precipitates of the M23 C6 type in the form of small rectangular plates, the dimensions of which are for instance on the order of 800A, or in the form of fish bones, the said structure displaying microdislocation regions surrounding the particles of the said precipitate, appearing in the form of long bands. The said examinations reveal neither ferrite nor carbide of the M 7 C 3 type.

Micrographic examination reveals that intergranular oxidation is considerably reduced as compared with the known refractory alloys considered as offering good resistance to oxidation in the hot state.

Forgeability, which is defined as the capability of a metal to be shaped through plastic deformation in the hot state without producing defects, may be determined in the case of refractory steels:

by rolling or forging an ingot for the manufacture of wires

by bending extruded tubes.

The steels of the present invention offer the best forgeability through rolling or forging under the following conditions:

maximum temperature during the heating 1,200°C
temperature at the end forging: $\geq 950^\circ\text{C}$.

They offer the best aptitude to deformation through bending under the following conditions:

heating temperature: 1,050° to 1,100°C

bending at $\geq 950^\circ\text{C}$, preferably from 1,050° through 1,100°C.

The refractory alloy according to the present invention may be in the state of moulded or centrifuged articles, parts or elements which are apt to be shaped in the hot state, as mentioned above, for instance by way of bending, forging, lamination or rolling.

The fact that centrifuged tubes may be bent in the hot state while at the same time holding good creep resistance, insensitivity to inter-granular corrosion, resistance to heat stress or fatigue and good weldability, renders the alloy of the present invention extremely interesting for specific uses in the above-mentioned range of temperatures (800°–1,250°C).

The above experimental results are confirmed by the excellent behaviour of the assemblies or parts made from alloys of the present invention, under particularly severe conditions (up to 1,250°C in oxidizing atmosphere for long periods of time).

According to a first embodiment, corresponding to an alloy well-adapted to be used in metallic parts outside a cracking and/or reforming furnace the composition is as follows:

Carbon	from	0.10	to	0.15	%	by wt.
Nickel	from	30	to	35	%	do.
Chromium	from	20	to	28	%	do.
Niobium	from	0.5	to	1.2	%	do.
Nitrogen	from	0.05	to	0.15	%	do.
Manganese	from	0.8	to	1.2	%	do.
Silicon	from	0.8	to	1.5	%	do.
Tantalum	from	0	to	0.3	%	do.
Molybdenum	from	0	to	0.5	%	do.
Titanium	from	0	to	0.20	%	do.
Aluminium	from	0	to	0.05	%	do.
Lead	from	0	to	0.01	%	do.
Tin	from	0	to	0.01	%	do.

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-Continued

Zinc	from	0	to	0.01	%	do.
Copper	from	0	to	0.25	%	do.
Phosphorous + sulphur				< 0.05	%	do.
Iron	complementary percentage					

In fact, for the above-mentioned use, the carbon content is preferably between 0.10 – 0.15 %, more particularly between 0.10 – 0.13 % since above 0.13 % the ductility may be insufficient and below 10 % the creep resistance may be insufficient (with Ni 30–33 %, Cr 20–23 %).

According to another embodiment of the present invention, the alloy has the following composition which is particularly suitable for constituting parts inside the cracking and/or reforming furnaces:

Cr	23	to	30	by weight
Ni	30	to	40	do.
Mn	0.6	to	1.50	do.
Si	1.0	to	1.8	do.
N	0.04	to	0.2	do.
(Nb + ½ Ta)	0.5	to	1.3	do.
Ti	0	to	1.00	do.
Mo	0	to	0.30	do.
S + P			≤ 0.05	do.

the contents of the other elements complying with the general disclosure of the composition of an alloy ac-

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C	0.10	by weight
Ni	33	do.
Cr	22	do.
Si	1	do.
Nb	1.1	do.
Mn	1	do.
N	0.05	do.
Ti	0.2	do.
Ta	0	do.
Mo	0	do.

Fe, impurities and other elements within the general range of the alloys according to the invention.

Investigation of creep resistance

Creep resistance tests have been carried out at temperatures comprised between 750° and 1,150°C during periods of time of from 100 to more than 10,000 hours, with a view to determining the resistance to rupture as a result of creeping of a 0.10 %-carbon nickel-chromium alloy with no addition of niobium and nitrogen in a first case and with simultaneous addition of niobium and nitrogen in a second case.

From the following table I it is seen that the value of the magnitude characterizing the creep resistance at 830°C is practically doubled by adding niobium and nitrogen, by comparing the centrifuged alloy C according to the invention with the centrifuged alloy B similar to C but containing neither niobium nor nitrogen.

Table I

N°	Sample	COMPOSITION				Creep resistance at 830°C		
		Ni	Cr	Nb	N	σ R 104h	σ R 105h	
A	laminated or rolled	33	21	—	—	1.8 hbar	1.1 hbar	
B	centrifuged	33	22	—	—	2.3 do.	1.5 do.	
C	centrifuged	33	22	1.1	0.06	4.5 do.	3.1 do.	

cording to the invention.

More preferably the following more limitative contents are used in said alloy:

C	0.10 to 0.15	by weight
Cr	24 to 28	do.
Ni	33 to 37	do.
Mn	0.8 to 1.2	do.
Si	1.2 to 1.5	do.
(Nb + ½ Ta)	0.6 to 1.2	do.
Ti	0.1 to 0.8	do.
N	0.05 to 0.15	do.

Example I

The following alloy C according to the invention is now considered:

Investigation of resistance to inter-granular oxidation

Since the effect of the increase in inter-granular oxidation is to reduce the time of rupture during a creep test, the time of rupture and the ultimate elongation of samples subjected to creep tests at 850°C have been determined in the following alloys B, C, C' and C'' for various values of stress.

Moreover, a micrographic examination of the broken samples has been effected on the one hand to verify the absence of intergranular oxidation and on the other hand to study the mode of rupture.

The results are shown in the following tables II and III.

Table II

N°	Sample	COMPOSITION				Creep results at 850°C		
		Ni	Cr	Nb	N	Stress hbar	Rupture time hours	Ultimate elongation %
B	centrifuged tube	33	22	—	—	5	54	2.0
B	do.	do.	do.	—	—	4	176	1.0
B	do.	do.	do.	—	—	3	662	<0.5
C	centrifuged tube	33	22	1.1	0.06	6	718	25
C'	do.	do.	do.	do.	do.	5	2 925	14
C''	moulded element	do.	do.	do.	do.	4	4 138	25

Table III

N°	COMPOSITION				Examination of broken samples	
	Ni	Cr	Nb	N	Intergranular oxidation	Mode of rupture
B	33	22	—	—	yes	intergranular without deformation
C	33	22	1.1	0.06	none	transgranular subsequent to deformation

It is first noted that the alloys C, C' and C'' according to the present invention, containing niobium and nitrogen, have a low carbon-content, of the order of 0.10 %, and their ultimate elongation is always at least equal to 10 %, in contradistinction to the alloys B having the same carbon-content but containing neither columbium nor nitrogen.

More generally, whatever the duration of the artificial "ageing" obtained with stress (or creeping) or without stress may be, the alloy according to the invention always has an ultimate elongation superior to 10 % as shown by numerous tests carried out by the applicant at temperatures comprised between 750° and 950°C.

It should also be noted that the alloy C according to the present invention displays no intergranular oxidation in the region of rupture of the samples, in contradistinction to the alloy B compared therewith.

It should also be pointed out that the absence of intergranular oxidation prevents embrittlement of the alloy and therefore increases the heat stress or fatigue, a fact that appears clearly from the following example.

Investigation of the heat stress or fatigue

The test carried out consisted in rapidly heating and cooling the edge of triangular-section samples.

The values measured or the criteria examined are as follows:

1. number of cycles leading to the initiation of a crack
2. crack extension rate
3. nature of crack

The results obtained are shown in the following table:

N°	COMPOSITION				Initiation Number of cycles (1)	Propagation (2)	Nature of crack (3)
	Ni	Cr	Nb	N			
B	32	22	—	—	50/60	3 mm after 100 cycles	intergranular
C	33	22	1.1	0.06	450/500	0.7 mm after 2500 cycles	transgranular

An intergranular crack, i.e. a crack extending between the grains, is an indication of brittleness of the alloy, whereas a transgranular crack is characteristic of good ductility and aptitude to mechanical consolidation; it is thus obvious that the alloy according to the invention retains good ductility and good mechanical properties subsequent to thermal ageing; otherwise stated, it therefore offers high resistance to heat stress or fatigue.

It is necessary to note that during the above-mentioned creep or fatigue tests, the samples were subjected to such stresses as to render rupture or cracking inevitable, whereas under industrial working conditions even as severe as those mentioned above for reforming and/or cracking furnaces, the stresses have neither the same intensity nor the same frequency.

In any case, the aforementioned tests show that the behaviour of the alloys B (or A) on the one hand and the alloys C according to the present invention, on the other hand, are quite different. The said tests reveal the favourable influence of simultaneous addition of niobium, silicon and nitrogen into an iron-base nickel-chromium alloy having a low carbon content.

Examples II and III

The alloys having the following compositions are particularly adapted to be used for very prolonged periods of time as inner construction parts or elements resisting to the severe conditions prevailing outside the reforming and/or cracking furnaces, that of Example II at a temperature of 800° to 1,000°C and that of Example III at a temperature of 1,000° to 1,150°C.

% by weight	Example II (*)	Example III (*)
C	0.11	0.11
Ni	33	33
Cr	22	25
Nb	1.0	1.0
N	0.06	0.06
Mn	1.0	1.0
Si	0.9	1.4
Ti, Mo	0	0
P + S	≤ 0.05	≤ 0.05

(*) the contents of the other elements particularly of impurities comply with the general disclosure of the composition of an alloy according to the invention.

Example IV

Another alloy according to the present invention has the following composition:

	%	by weight
C	0.10	do.
Cr	25	do.
Ni	33	do.
Mn	1	do.
Si	1.5	do.
(Nb + ½ Ta)	1.2	do.
N	0.10	do.
Ti	0.1	do.
Mo	0.2	do.
S + P	≤ 0.05	do.
Fe and impurities : complementary percentage		

Example V

Another alloy according to the present invention has the following composition:

	%	by weight
C	0.12	do.
Cr	25	do.
Ni	35	do.
Mn	1	do.
Si	1.5	do.
(Nb + ½ Ta)	0.7	do.
N	0.08	do.
Ti	0.3	do.
Mo	0.20	do.
S + P	≤ 0.05	do.
Fe and impurities : complementary percentage		

Examples VI to VIII

Said alloys are particularly adapted to be used for constituting inner metallic parts of cracking and/or reforming furnaces.

% by weight	Example VI (*)	Example VII (*)	Example VIII (*)
C	0.08	0.18	0.06
Ni	30.0	33.5	39.0
Cr	20.5	29	28.8
Nb	0.8	1.0	0.35
N	0.16	0.05	0.04
Mn	1.2	2.0	1.8
Si	0.9	1.8	1.95
Mo	0.2	0.4	0.38
Ti	0.1	0	0.10
P + S	≤ 0.05	≤ 0.05	≤ 0.05

(*) the contents of the other elements particularly of impurities comply with the general disclosure of the composition of an alloy according to the invention.

Of course the invention is by no means limited to the forms of embodiment described and illustrated, which have been given by way of example only. In particular, it comprises all the means constituting technical equivalents to the means described as well as their combinations, should the latter be carried out according to the spirit of the invention.

What is claimed is:

1. Refractory iron-base alloy offering high resistance to creep, thermal shocks, heat fatigue and intergranular oxidation, as well as good weldability, consisting essentially of the following elements in the following weight proportions:

C	0.05	%	0.20
Ni	30	-	40
Cr	20	-	30
Nb	0.2	-	2
N	0.04	-	0.2
Mn	0.6	-	2
Si	0.6	-	2
Ta	0	-	0.3
Ti	0	-	1
Mo	0	-	0.5
Al	0	-	0.05
Pb	0	-	0.01
Sn	0	-	0.01
Zn	0	-	0.01
Cu	0	-	0.25

and the balance essentially iron and wherein the weight proportions of the aforesaid elements comply with the following formulas:

$$30 \times C \% + Ni \% + 0.5 \times Mn \% + 16 \times N \% = Cr \% \pm 0.5 \times (Nb + 1/2 Ta) \% + 3.5 \times Ti \% + 1.5 \times Si \% + Mo \% + 11 + 2\%$$

$$A = B \pm 20\%$$

with $A = 30 \times C \%$

$$B = 2 \times Ti \% + 6 \times (Nb + 1/2 Ta) \%$$

2. Alloy according to claim 1 wherein the weight proportion of niobium added to half the weight proportion of tantalum is at least equal to six times the proportion of carbon.

5 3. Alloy according to claim 1 wherein the weight proportion of titanium is substantially twice that of carbon.

4. Alloy according to claim 1 containing the following elements in the following weight proportions:

C	0.10	%	0.15
Ni	30	-	35
Cr	20	-	28
Nb	0.5	-	1.2
N	0.05	-	0.15
Mn	0.8	-	1.2
Si	0.8	-	1.5
P + S		-	≤ 0.05

5. Alloy according to claim 1 containing, by weight, 0.10 - 0.13 % of carbon, 30 - 33 % of nickel and 20 - 23 % of chromium.

6. Alloy according to claim 1 containing the following elements in the following weight proportions:

C	0.05	%	0.20
Ni	30	-	40
Cr	23	-	30
(Nb + 1/2 Ta)	0.5	-	1.3
N	0.04	-	0.2
Mn	0.6	-	1.5
Si	1.0	-	1.8
Ti	0	-	1.0
MO	0	-	0.30
P + S		-	≤ 0.05

7. Alloy according to claim 1 containing the following elements in the following weight proportions.

C	0.10	%	0.15
Ni	33	-	37
Cr	24	-	28
(Nb + 1/2 Ta)	0.6	-	1.2
N	0.05	-	0.15
Mn	0.8	-	1.2
Si	1.2	-	1.5
Ti	0.1	-	0.8
Mo	0	-	0.30
P + S		-	≤ 0.05

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,833,358

DATED : September 3, 1974

INVENTOR(S) : Jean Bellot and Michel Hugo

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

Column 9, line 44, after "Cr %", the symbol " $\pm$ "
should read -- + --; line 46, after "11", the symbol "+"
should read -- $\pm$ --.

Signed and Sealed this

Twenty-seventh Day of September 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks