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PROCESS AND PRODUCT FOR IMPROVED RESISTANCE TO STRESS CORROSION

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6 Claims. (Cl. 138—177)

This application is a continuation-in-part of copending application Ser. No. 321,027, filed Nov. 4, 1963, and now abandoned.

The present invention is directed to metal products having improved resistance to stress corrosion and a process for the preparation of said products.

As used herein, the term "stress corrosion" is defined in the broad sense to include corrosion which occurs during the application of externally applied stress and also situations wherein no external stress is applied. When applied, the external stress can be continuous or intermittent and can vary in magnitude.

Steel and other metals play an important part in the production, refining and processing of petroleum. Many of the applications of metals in the petroleum industry involve corrosive environments. This is particularly true in the production of crude petroleum where environments are encountered which contain brines, that is, various metal halides, and in particular, sodium chloride; sulfur-containing compounds, such as hydrogen sulfide; carbon dioxide; organic acids and other corrosive materials. Often these corrosive materials are present in the crude petroleum or, if not, are present in the formations which are adjacent the petroleum-producing zones. The problems of corrosion and how to combat it are particularly important to manufacturers of well casing and tubing which are employed in connecting the ground surface with the oil-bearing formations and to the manufacturers of sucker rods or oil well pump rods which are employed in conjunction with pumps which affect removal of crude petroleum through oil well casing. These "sucker rods" are steel rods which come in various diameters, usually 25 or 30 feet in length, having threads or other means at each end whereby the rods can be coupled together to form a "string" of sufficient length to extend from the pump driving means which is stationed above ground down to the oil well pump which is located down near the oil-producing formation.

Sucker rods are ordinarily made from carbon or low alloy steels and are installed in service without any special treatment other than heat treatment such as normalizing or tempering. It is recognized that mill scale-bearing surfaces are undesirable, and some of the manufacturers treat the sucker rods to remove hard mill scale by flame treatment or, more commonly, by shot blasting or shot peening. These various processes for removing mill scale have been followed for up to fifty years or more. In general, these processes succeed in removing most but not all of the mill scale.

At the present time, the life expectancy of sucker rods is relatively short and in highly corrosive environments such as those containing a large amount of hydrogen sulfide, failure may occur in a very few months or even in

a shorter time. Failures also occur at a very high rate in services wherein the stresses placed on the sucker rods in the pumping operation are very high. While not subject to externally applied stresses like the sucker rods, well casing and tubing also experience in corrosive environments a much shorter life than would be obtained in the absence of corrosive materials.

It is an object of this invention to provide an improved process for reducing the failure of metals due to stress corrosion.

It is another object of this invention to provide an improved process for treating the surface of metals to increase their resistance to stress corrosion.

Still another object of this invention is to provide metal products having improved resistance to stress corrosion by a novel method of surface treatment.

Yet another object of this invention is to provide sucker rods and tubular goods having improved resistance to stress corrosion.

These and other objects of the invention will become more readily apparent from the following detailed description and discussion.

The foregoing objects are achieved broadly by providing metal products from which substantially all oxide-defective and decarburized surface layers have been skinned off the metal surface by a mechanical treatment and the surface thereafter subjected to surface cold-working to induce compressive stresses in the metal surface. The oxide-defective and decarburized surface layers are those which are formed on the metal usually either during manufacture or during subsequent heat treatment.

In the drawings:

FIGURE 1 shows in graphical form the relationship between reduction in diameter and depth of cold-working for A.I.S.I. 1036 steel.

FIGURE 2 shows the results of fatigue tests pertinent to the invention.

FIGURE 3 is another graphical illustration of fatigue tests pertinent to the invention.

In one aspect, the invention is directed to improved sucker rods and their method of preparation. In another aspect, the invention is directed to improved tubular goods and their method of preparation; such as, drill pipe, which is employed in drilling wells and in particular, wells for the production of hydrocarbons; tubular casing, which is employed in wells to retain the formation and through which petroleum products can be produced; production tubing, which can be disposed within the well casing for producing a plurality of formations; and line pipe which is employed for movement of petroleum above ground, for example, in gathering systems.

While it is realized that the individual steps of removing surface oxides and decarburized layers from metals by mechanical treatment and surface cold-working of metals are both very old in the art, it has been found unexpectedly that the combination of these two treatments provides a surface which has substantially greater resistance to stress corrosion than the ordinary metal surface. This finding is particularly unexpected when one considers that stress corrosion, particularly that which occurs in an environment of hydrogen sulfide, has been considered by many to be aggravated by stresses introduced in the surface of metals, for example, by surface cold-working. In addition, skinning-off metal oxides and decarburized layers to expose the bare metal surface per se would not be expected to provide a material having enhanced resistance to stress corrosion. Yet, as stated, the combination of these two operations has unexpectedly provided a very substantial improvement in corrosion resistance.

In carrying out the process of this invention, the skinning off process by which the oxide-defective and decarburized layers are removed can be effected by any mechanical means, for example, by a cutting or machining operation, by milling, by grinding, or by any other mechanical operation which assures substantially complete removal of oxides and decarburized layers and preferably, in the case of sucker rods or well casing, resulting in a product of substantially uniform cross section. This metal removal process generally involves an operation to a depth of from 0.002 to about 0.010 inch and preferably, not greater than about 0.015 inch. Examination of the metal for effective oxide and decarburized layer removal can be made visually or with a suitable scanning device for a continuous commercial operation.

The second step of the process, the surface cold-working, is effected in such a manner so as to impart compressive stresses, preferably of a substantially uniform nature, in the surface of the metal. These stresses can be provided in any of the conventional manners by the employment of either constant or impact tooling, such as, shot peening, cold-rolling, cold-drawing, and swaging. Surface cold-working can provide tensile stresses as well as compressive stresses, therefore, it is important that the cold-working be carried out in such a manner as to assure the desired compressive stresses. The surface cold-working can be employed in varying degrees depending on the particular metal involved. Generally, it is carried out in such a manner as to provide cold-worked surface layers of a depth ranging from about 0.001 inch to as high as 0.02 inch or higher. The compressive stresses involved will range in magnitude from as low as 100 p.s.i. to as high as 50,000 p.s.i. or higher.

The process of producing cold-worked surface layers involves a reduction in thickness of the material being treated which differs in magnitude from the depth of cold-working. Usually, the reduction in thickness, expressed as reduction in diameter, is from about 0.25 to about 0.45 times the depth of cold-working. The relationship between reduction in diameter and depth of cold-working for A.I.S.I. 1036 steel is shown in FIGURE 1 of the drawings.

While the process of treatment as described herein is referred to as "cold-working," this treatment can be effected over a range of temperatures which can be subatmospheric, for example −20° F. or −30° F. or lower, extending upwardly, for steels, to as high as about 950° F. The temperature of cold-rolling as defined herein is the temperature at which the surface treatment is initiated, for example, cold-rolling at atmospheric temperature indicates no heating or cooling of the work piece prior to cold-rolling. During the cold-rolling operation, of course, heat is generated due to the work input to the metal which ordinarily results in an increase of the temperature of the work piece. In any case, the cold-working actions herein refer to temperatures which do not produce appreciable by-product annealing and/or grain growth but which leave the grains in a strained condition.

The pressure employed during cold-working will depend on the type of means used for effecting this treatment and the depth and rapidity of the cold-working operation. Pressure is not critical and any amount required to effect the cold-working can be employed.

Steels are the principal metals of construction employed in the oil industry, therefore, the invention finds particular application in the ferrous metals and particularly steels. More preferably, the invention is directed to non-austenitic steels, that is, those of a pearlitic or ferritic structure. In addition to steels, the invention also finds applications to other metals and metal combinations, that is, alloys, which in their preparation or processing have obtained an oxide-defective and decarburized surface layer. Some examples of other metals and alloys which come within the scope of the invention are those involving K-Monel, nickel, copper, aluminum, cobalt, titanium, zirconium, vanadium, iron, rhodium, platinum and the like.

Sucker rods are normally prepared from solid bar stock, therefore, the improvements contemplated by this invention are carried out on the outer surface of the sucker rods. It is possible, however, that for some services a hollow sucker rod might be desirable, for example, when it is desired to introduce a corrosion inhibitor or some other material to a pumping well. In this event, it is contemplated that the process of the invention can also be applied to the inner surface through the use of appropriate mechanical metal removal means and means for surface cold-working to apply the desired compressive stresses. In the case of oil well tubular goods (drill pipe, casing, production tubing, line pipe, etc.), the process of the invention can be applied to either the outer surface or the inner surface of the metal, or both, if desired.

The following examples are presented in illustration of the invention.

Example I

Thirty fatigue samples were cut from one piece of ¾-inch Axelson "60" sucker rod. Axelson "60" is a fully normalized rod that is made of A.I.S.I. 1036 steel. (This rod is labeled rod A in Table I.) The specimens were turned down with a lathe to a diameter of approximately 0.50 inch. A gage section was provided in the middle of each specimen having a radius of curvature of 0.5 inch and a minimum thickness of 0.30 inch.

The thirty fatigue specimens were sanded circumferentially with #1 paper until all of the tool marks were removed. Then they were normalized in the laboratory furnace. They were heated to 1650° F. for one hour and then air cooled. This heat treatment left a black oxide (Fe_3O_4) scale on the samples.

After the samples were normalized, six of them were tested in R. R. Moore Rotating Beam Fatigue Machines at approximately 1725 r.p.m. without disturbing the black oxide coating. The results of this test are shown in FIGURE 2 on the curve labeled "Scale Present."

The remaining twenty-four samples were sanded circumferentially with #1 grit paper until the scale decarburized material was removed. (Each specimen was examined with a low power microscope to ascertain that the scale and decarburized material was removed.) Eight of these specimens were then tested in the fatigue machines, and the results are shown in FIGURE 2 on the curve designated "Descaled."

Six of the remaining specimens were cold-worked with ½-inch balls. The balls were rotated around the center of the gage section of the sample. By using a tapered cone, the balls were forced into the sample as they rotated. The samples were cold-worked until their diameter was reduced by 0.010 inch. This produced a cold-worked band that was about 3/32 of an inch wide. When these specimens were run in the fatigue machines, an increased performance was observed, but all specimens broke *outside* of the cold-worked area in a larger diameter section. (The stress is inversely proportional to the diameter.) The results of these tests are shown in Table I.

The depth of the cold-working was measured microscopically to be about 0.020 inch.

The remaining ten specimens were cold-worked with one-inch balls to produce a cold-worked band throughout the entire gage section. The reduction of the diameter was measured to be about 0.010 inch. The specimens were then tested in the fatigue machines with the results being shown on the curve "Descaled and Cold-Worked" in FIGURE 2.

The fatigue tests were conducted in air. Brine (3 percent NaCl in distilled water) was dropped on the center of the sample at a rate that was sufficient to keep it wet. The samples were tested at pressures varying from 20,000 to 50,000 p.s.i., i.e., approximately the normal working stress levels for oil well pumping rods. Usually three samples of each set were tested at each stress level.

Subsequently, additional samples were prepared from another A.I.S.I. 1036 steel sucker rod. This set of specimens was from one, ⅝-inch diameter, Oilwell, Type N rod. (The Oilwell rod is labeled rod B in Table I.) This grade rod was also normalized at the factory as a standard manufacturing procedure.

The fatigue performance of this rod (descaled, 3 percent NaCl) was checked by running one sample at each of the following stress levels: 20,000, 30,000 and 40,000. It was run as nearly as possible under the same conditions as the descaled Axelson "60" rod, and its aerobic corrosion fatigue behavior was close to the performance of the Axelson rod. The results of these tests are also shown in Table I.

Example II

Fatigue samples from the Oilwell rod of Example I were treated in the following manner.

(1) All specimens were sanded circumferentially with #1 grit paper.

(2) Twelve specimens were cold-worked with one-inch diameter balls. The one-inch balls cold-worked the entire gage section. The diameter was reduced by 0.010 inch.

(3) Three of the non-cold-worked specimens were tested in the fatigue machine at 20,000 p.s.i. and three were tested at 30,000 p.s.i. These specimens were tested in 3 percent NaCl saturated with H_2S. During the test, the sample was enclosed in a sealed container which made the system fairly air free.

(4) Two of the cold-worked samples were tested in the H_2S anaerobic system at 20,000 p.s.i., and they ran 50,000,000+ cycles without breaking. Three of them were tested at 30,000 p.s.i. and two of them ran 12,000,000+ cycles. Both samples broke outside of the sealed enclosure where the stress was substantially lower, but where air and a small amount of H_2S and brine were present. The third sample ran 22,367,000 cycles and broke in the gage area.

The results of these tests are shown in FIGURE 3. Hardness tests were carried out on one specimen on two Rockwell ranges with the following results. (The specimen was from rod B.)

Cold-worked area:

Rockwell	A 60.5
Rockwell	A 60.4
Rockwell	A 59.9
Average	A 60.1
Rockwell	B 94

Non-cold-worked area:

Rockwell	A 54
Rockwell	A 54
Rockwell	A 54
Average	A 54
Rockwell	B 87
Rockwell	B 85
Average	B 86

This shows a consistent increase in hardness in the cold-worked area.

All of the data obtained in Examples I and II are presented in numerical form in Table I.

TABLE I

Stress	Cycles						
	Scale Present	Descaled			Descaled and Cold-Worked		
	3% NaCl (Rod A)	3% NaCl (Rod B)	3% NaCl (Rod A)	3% NaCl+H_2S (Rod B)	3% NaCl[1] (Rod A)(½" Balls)	3% NaCl (Rod A)(1" Balls)	3% NaCl+H_2S (Rod B)
20,000	2,497,000 1,089,000 1,771,000	2,340,000	3,020,000 4,045,000 2,055,000	5,018,000 [3] 550,000 6,618,000	6,092,000 6,000,000 11,255,000	37,863,000 31,430,000 34,224,000	[2] 50,549,000 [2] 62,020,000
Average	1,786,000		3,040,000	5,818,000	7,782,000	34,506,000	
30,000	761,000 799,000 596,000	1,158,000	1,072,000 1,614,000 831,000	5,684,000 3,223,000 2,599,000	3,141,000 4,681,000 6,599,000	23,225,000 10,194,000 14,127,000	[4] 14,249,000 [4] 12,368,000 22,367,000
Average	719,000		1,172,000	3,835,000	4,807,000	15,849,000	16,328,000
40,000		269,000	350,000			14,068,000 11,987,000	
Average						13,027,000	
50,000			87,000			7,660,000 5,278,000	
Average						6,469,000	

[1] The ½" balls cold-worked a short length of the gage section and all samples broke outside of the cold-worked area.
[2] Sample did not break, but it was cracked
[3] This sample is not included in the average.
[4] Sample broke outside of the gage section.

It is noted from the data in Table I that the removal of scale from the specimens provided an increase in fatigue life (cycles before failure) ranging from about 25 to 60 percent in the presence of sodium chloride. Further treatment (cold-working with 1-inch balls) of the descaled specimens provided an increase in life over the untreated specimens from about 1800 to 2100 percent in the sodium chloride atmosphere.

It is particularly surprising that substantial improvement in fatigue life is obtained in the corrosive environment containing hydrogen sulfide which is generally held to be much more damaging than an environment of sodium chloride alone. Normally, when steels increase in hardness, there is an increased hydrogen sulfide cracking susceptibility.

Example III

Three additional specimens of the Oilwell rod (rod B) were prepared following the procedure previously described. The specimens were tested at 30,000 p.s.i. in anaerobic H_2S and CO_2 with the following results:

TABLE II

Stress (p.s.i.)	Reduction In Diameter, inch	Cycles	
		Cold-worked	Non-Cold-worked
30,000	0.0117	17,933,000	4,403,000 2,120,000

Example IV

Twelve additional specimens of the Oilwell rod (rod B) were prepared following the procedure previously described. The specimens were cold treated to different depths and then were tested at 20,000 and 30,000 p.s.i. in aerobic 3 percent NaCl. The results of the test are shown in Table III.

TABLE III

Stress (p.s.i.)	Reduction Of Diameter, inch	Cycles	Reduction Of Diameter, inch	Cycles
20,000	0.0075	17,169,000	0.0171	20,525,000
20,000	0.0091	17,766,000	0.0183	35,619,000
20,000	0.0086	15,135,000	0.0192	25,950,000
Average	0.0084	16,690,000	0.0182	27,365,000
30,000	0.0069	5,664,000	0.0183	17,444,000
30,000	0.0059	6,765,000	0.0178	13,132,000
30,000	0.0061	4,740,000	0.0188	13,134,000
Average	0.0063	5,723,000	0.0183	14,570,000

The results of this example show that cold-working to a depth of about 0.021 inch (reduction in diameter from 0.0171 to 0.0192 inch) provides substantially improved performance over a lower amount of cold-working, namely, to a depth of about 0.017 inch (reduction in diameter from 0.0059 to 0.0091 inch).

Example V

Additional specimens were prepared from K-Monel in dimensions corresponding to those set forth in Example 1. These specimens were sanded and annealed at 1300° F. followed by a water quench. Half of them were cold-worked to a depth of 0.015 inch (reduction in diameter 0.010 inch) and were then tested at 30,000 p.s.i. in aerobic 3 percent NaCl. The results of these tests are presented in Table IV.

TABLE IV

Stress (p.s.i.)	Cycles	
	Cold-Worked	Non-Cold-Worked
30,000	11,821,000 17,940,000 9,233,000	7,952,000 3,355,000 3,880,000
Average	12,998,000	5,064,000

It is apparent from the data in Table IV that greatly improved life under corrosive conditions is also obtained by treating a metal other than steel in accordance with the process of this invention.

The reasons for the great improvement in resistance to stress corrosion obtained by the process and products of this invention is not readily apparent. For example, as pointed out previously, sucker rods have been treated by shot peening which would induce compressive stresses in the surface of the rods. Rods treated in this manner, however, have been shown by tests to be not substantially better than untreated rods. Thus, it appears that the descaled step of the present invention is of major importance even though this step per se does not provide a significant improvement in resistance to stress corrosion. Since removal of scale and decarburized layers is so important, it is possible that previous methods of treatment such as shot peening have been ineffective in their failure to remove substantially all of the oxide scale and decarburized layers from the metal surface. In any event, notwithstanding any speculations as to the reasons for the improvement obtained, it is apparent that the combined oxide and decarburized layers removal and cold-working steps of the present invention result in major improvements in resistance of metals to stress corrosion.

Although this invention has been described with respect to particular embodiments thereof, it is not to be so limited as changes and modifications may be made therein which are within the spirit and scope of the invention as defined by the appended claims.

We claim:

1. A process for the treatment of a steel sucker rod for use in corrosive environments containing hydrogen sulfide which comprises skinning-off by mechanical treatment substantially all oxide-defective and decarburized surface layers and thereafter inducing compressive stresses in the surface of said sucker rod by surface cold-working.

2. Sucker rods prepared in accordance with the process of claim **1**.

3. The process of claim **1** in which the cold-working is effected to a depth not exceeding about 0.020 inch.

4. A process for the treatment of steel oil well piping for use in corrosive environments containing hydrogen sulfide which comprises skinning-off by mechanical treatment substantially all oxide-defective and decarburized surface layers and thereafter inducing compressive stresses in the surface of said oil well piping by surface cold-working.

5. Oil well piping prepared in accordance with the process of claim **4**.

6. The process of claim **4** in which the cold-working is effected to a depth not exceeding about 0.020 inch.

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PROCESS AND PRODUCT FOR IMPROVED RESISTANCE TO STRESS CORROSION

Filed Aug. 3, 1964 3 Sheets-Sheet 1

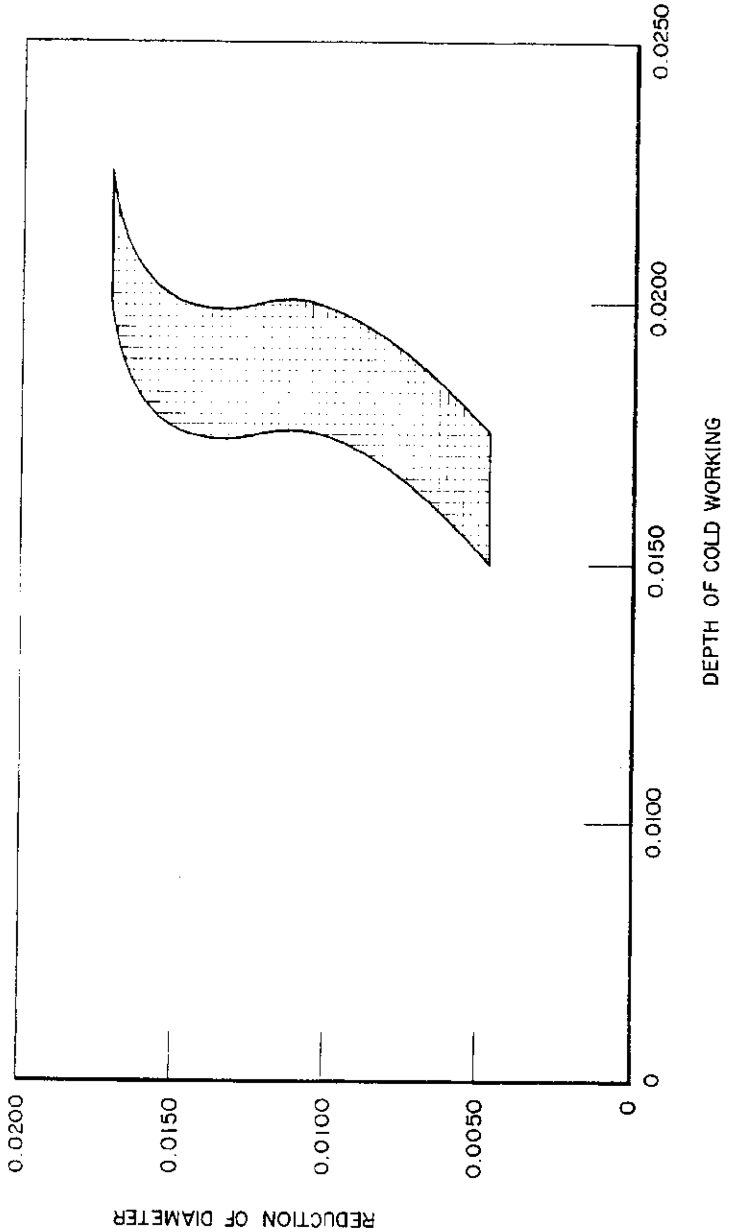

FIG. 1

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PROCESS AND PRODUCT FOR IMPROVED RESISTANCE
TO STRESS CORROSION

Filed Aug. 3, 1964 3 Sheets-Sheet 2

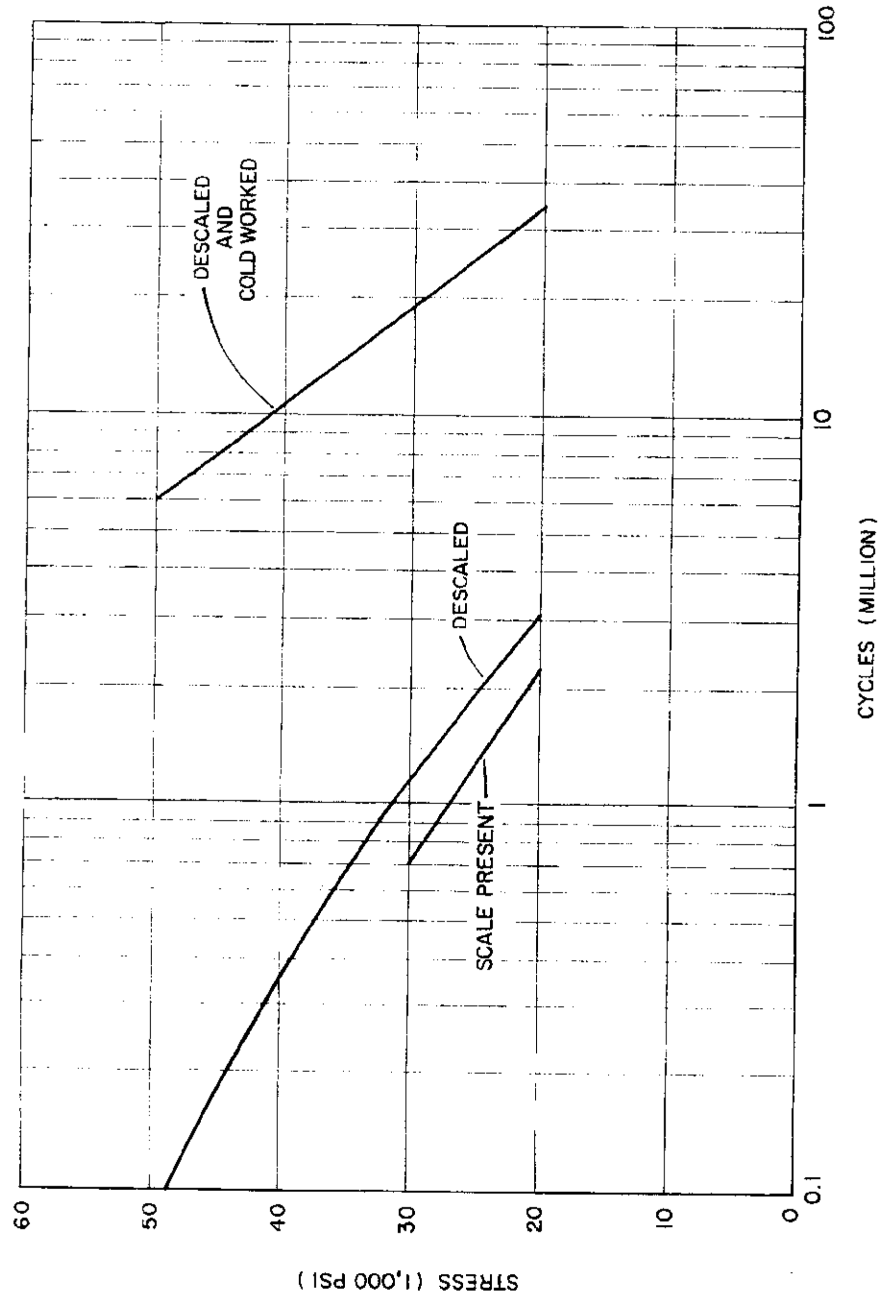

FIG. 2

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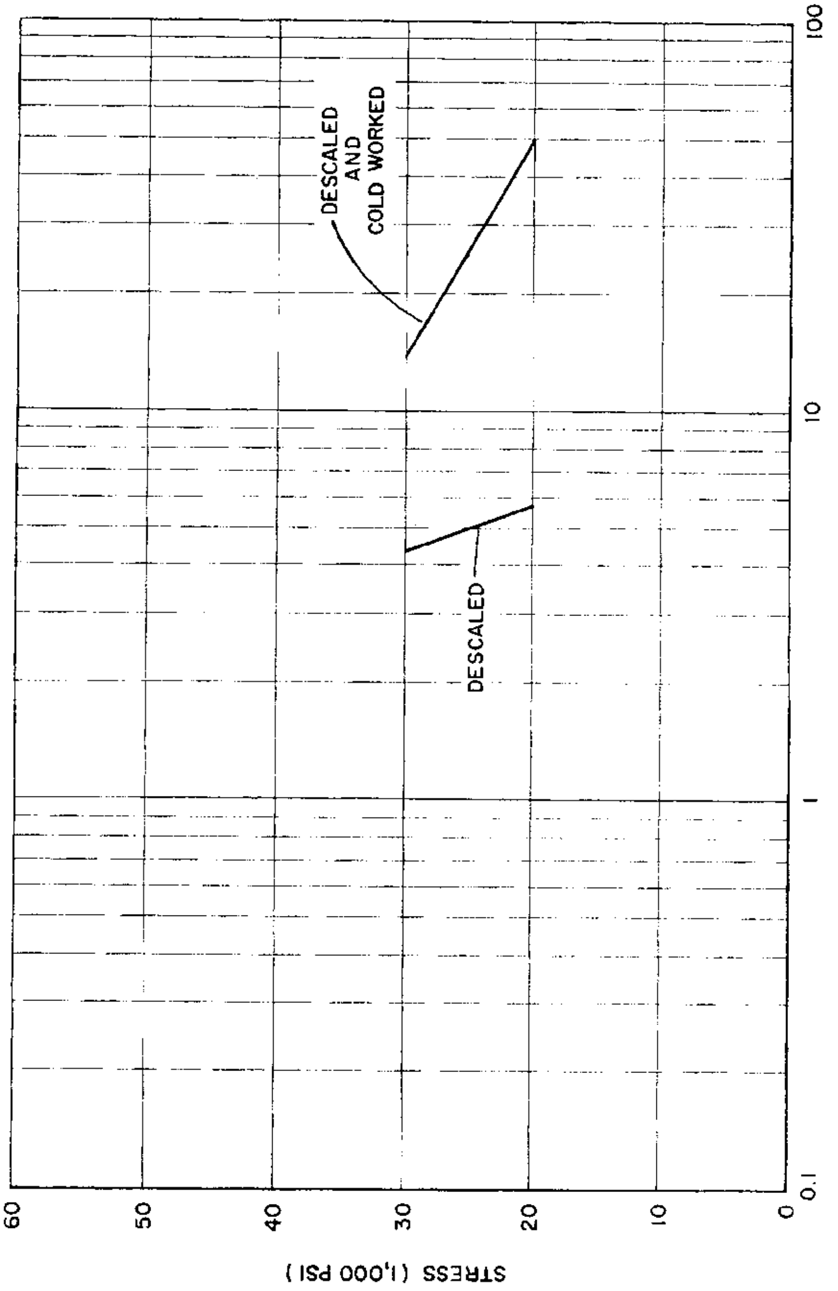

FIG. 3

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Frederick J. Radd et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 54, for "1300° F." read -- 1600° F. --.

Signed and sealed this 14th day of January 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents