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P. G. BASTIEN
PROCESS FOR IMPROVING STRESS CORROSION CRACKING
RESISTANCE OF ALLOYED STEEL IN HYDROGEN
SULPHIDE ATMOSPHERE

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2 Sheets-Sheet 1

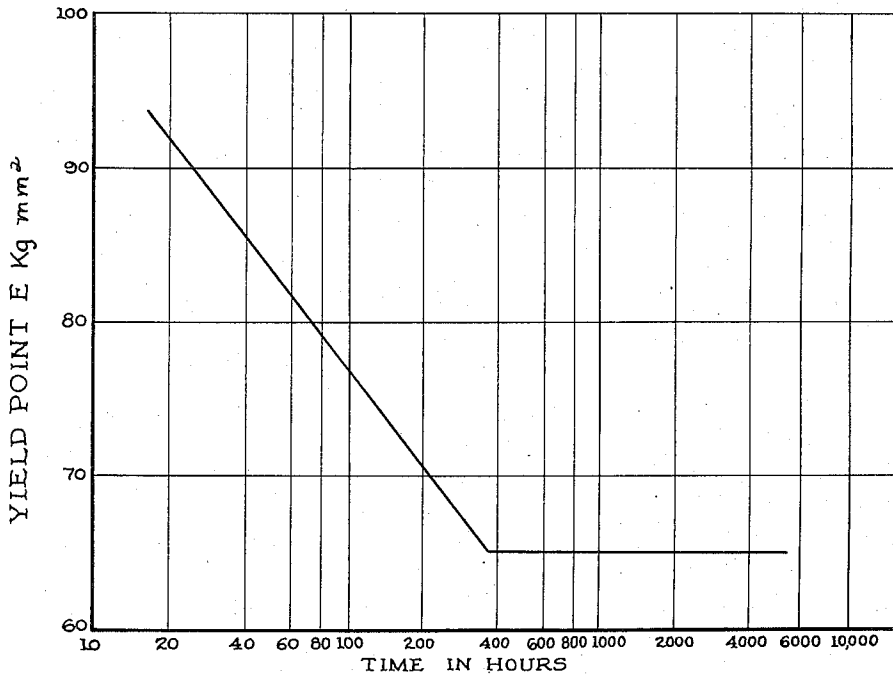
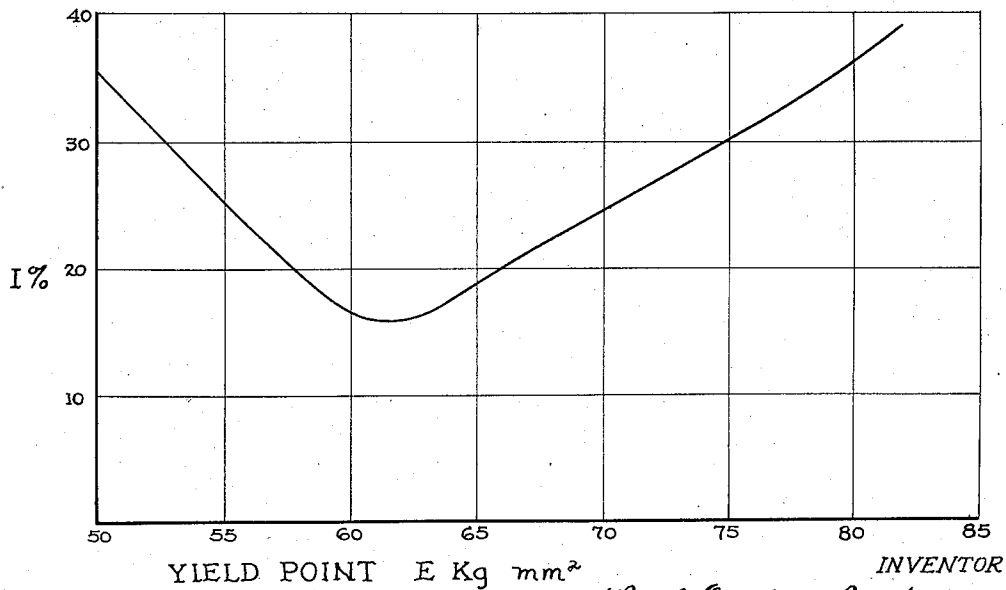


FIG. 1. TESTS OF STRESS-CORROSION CRACKING WITH HYDROGEN SULFIDE

FIG. 2. RELATIVE REDUCTION IN AREA BY HYDROGENATION



YIELD POINT E Kg mm²

INVENTOR

Paul Gaston Bastien,

BY

Cameron, Kerkam & Sutton

ATTORNEYS

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AREA OF UTILITY OF STEEL IN THE PRESENCE OF HYDROGEN SULFIDE
FIG.3.

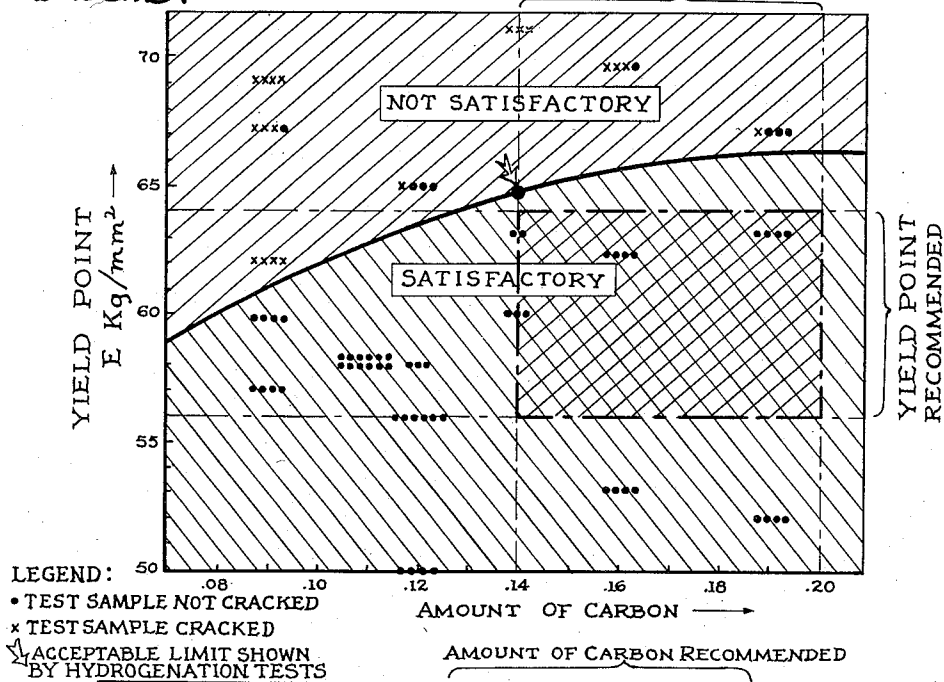
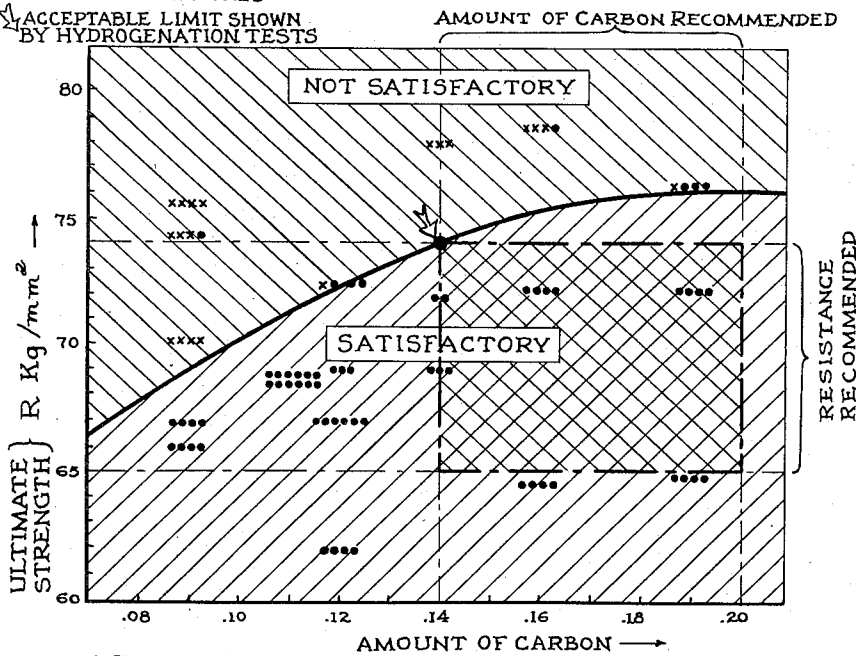


FIG.4.

Paul Gaston Bastien,

BY
Cameron, Kerkam & Sutton
ATTORNEYS

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2,895,861

**PROCESS FOR IMPROVING STRESS CORROSION
CRACKING RESISTANCE OF ALLOYED STEEL
IN HYDROGEN SULPHIDE ATMOSPHERE**

Paul Gaston Bastien, Paris, France, assignor to Société
des Forges et Ateliers du Creusot, Paris, France, a
company of France

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7 Claims. (Cl. 148—21.5)

This invention relates to the manufacture of elements from alloyed steel, and is more particularly concerned with the manufacture of parts possessing superior tensile properties and required to withstand cracking due to stress corrosion in a moist atmosphere of hydrogen sulfide, in the presence or absence of carbonic gas, and generally in a medium conducive to embrittlement of the steel by hydrogen.

In the course of well drilling operations for the recovery of petroleum or natural gas, for example, the tubes used for this purpose often come in contact with a moist and hot medium charged with hydrogen sulfide under pressure. Also the parts of steel employed in installations for treating petroleum products or natural gas, may come into contact with a liquid or gaseous medium that causes embrittlement of the steel, as for example a medium more or less saturated with hydrogen sulfide under pressure and at temperatures often in excess of the ambient temperature.

These conditions are very detrimental to the steel in that they give rise, after a more or less extended period, to the formation of cracks resulting from the superposition of mechanical stresses and the embrittlement induced by the hydrogen arising from the corrosion by hydrogen sulfide.

It has been found that the cracks in most cases resulted from a structure of insufficiently stable metal, comprising particularly incompletely tempered martensite or residual austenite dispersed throughout the mass.

Moreover, especially for application in well bores of great depth for the recovery of petroleum or natural gas, it is indispensable to obtain steel possessing superior tensile properties.

In order to avoid cracking, attempts have been made to use steels that heretofore presented difficulties in manufacture and particularly in the treatment thereof. On the other hand, the problem of obtaining superior tensile properties has remained, for the time being, difficult to solve, especially when it comes to producing a steel that will continuously withstand the formation of cracks.

The present invention makes it possible to obtain a steel having satisfactory tensile properties which is capable of resisting cracking in the presence of hydrogen sulfide even under pressure and at temperatures in excess of the ambient temperature.

It has been found that it is possible to employ a steel of the chromium-molybdenum-vanadium type confined heretofore to uses in other fields, on condition that it is subjected to a treatment especially chosen in contemplation of the particular conditions encountered during the use thereof referred to above.

According to the invention, the process comprises the utilization of a steel having the following composition by weight:

	Percent
C -----	0.10 to 0.25
Si -----	0.10 to 0.50
Mn -----	0.30 to 1.0

2

	Percent
Cr -----	1 to 14
Mo -----	0.4 to 1.5
V -----	0.10 to 0.60
5 Ni -----	0 to 1

the remainder being substantially all iron except for minor quantities of other elements such as sulfur up to 0.030%, phosphorus up to 0.025%, copper up to 0.20%, and a two-stage thermal treatment of this steel. The first stage of the heat treatment consists in an austenitization at a temperature from 975° to 1100° C. for a period of about one hour or less (from 1 to 5 minutes in the case of tubes), followed by a cooling step (hardening) 10 conducted at an average speed at least equal to 30° C. per minute between 850° and 600° C., and the second stage consists in tempering at a temperature from 725° to 800° C. for a period producing a yield point between 55 and 65 kg./mm.².

20 It has been found that the yield point E should not be greater than 65 kg./mm.² for steel which is resistant to stress corrosion cracking in the presence of hydrogen sulfide as shown by the curve of Figure 1. From this figure it is seen that the time required for cracking in- 25 creases as the yield point decreases.

The relative reduction in area (percent) by hydrogenation increases as the yield point decreases or increases from optimum values between 58 and 65 kg./mm.² as is seen in Fig. 2.

30 When the steel is employed in tubes the two heat treatments described above are applied after the tubes are formed.

According to the invention, it is thus contemplated to use a hardenable steel which can endure a tempering 35 treatment at high temperature while still preserving its superior tensile properties, and having imparted thereto a thermodynamically stable structure necessary for stress corrosion cracking resistance.

The tensile properties of this stable structure, such 40 as the value of R which is the ultimate strength applied, and the yield point define the area of utility of these chrome-molybdenum-vanadium steels as a function of the amount of carbon as shown in Figs. 3 and 4.

The invention will now be described in greater detail 45 with reference to specific examples.

Example I

Test pieces were made from a steel having the follow- 50 ing composition by weight:

	Percent
C -----	0.17
Si -----	0.30
Mn -----	0.50
55 Cr -----	2.5
Mo -----	1
V -----	0.25
Ni -----	0.2
S -----	0.02
60 P -----	0.015
Fe -----	Remainder

This steel is intended for contact with a saturated solution of hydrogen sulfide.

65 It was subjected to the following treatment:

First treatment stage: Austenitization at a temperature of from 980° to 1000° C. for about one hour, followed by air cooling (hardening) at an average speed at least equal to 30° C. per minute between 850° and 70 600° C.

Second treatment stage: Tempering at a temperature of approximately 750° C. for about one hour.

3

The tensile properties thus obtained are as follows:

Yield point ----- $E=62 \text{ kg./mm.}^2$.
 Ultimate strength --- $R=72 \text{ kg./mm.}^2$.
 Elongation ----- $A=24\%$ (the useful length of the
 test piece being equal to four
 times its diameter).

The structure of the steel treated in the above manner is composed of fine spheroidized carbide particles uniformly distributed in the ferritic matrix. Such a structure becomes readily apparent when it is subjected to the action of an alcohol solution of picric acid.

The steel treated in this manner was tested in contact with a saturated solution of hydrogen sulfide containing 0.5% by volume of acetic acid, the latter functioning to accelerate and aggravate the corrosion. The metal was submitted to a permanent flexure when using a two point beam loaded specimen, the maximum stress being slightly higher than the yield point of the metal under flexure. No cracks were observed after 3000 hours of this treatment.

On the other hand, in the case of tempering temperatures below 725°C. or too short tempering periods which impart to the metal a yield point above 65 kg./mm.^2 , fractures were obtained in less than 500 hours.

Example II

Test pieces were obtained in a steel having the following compositions by weight:

	Percent
C -----	0.14
Si -----	0.14
Mn -----	0.45
Cr -----	2.49
Mo -----	0.90
V -----	0.22
S -----	0.011
P -----	0.020
Fe -----	Remainder

This steel was subjected to the following treatment:

First treatment stage: Austenitization at 980°C. followed by air cooling (one half hour).

Second treatment stage: Tempering at a temperature of 725°C. for one hour.

The yield point of the steel was $E=71.2 \text{ kg./mm.}^2$.

This steel was placed in contact with a saturated solution of sulfuric acid and maintained under flexure. A crack developed after 112 hours and two cracks developed in 300 hours.

A steel of the same composition was subjected to the following treatment:

First treatment stage: Austenitization at 980°C. followed by air cooling (one half hour).

Second treatment stage: Tempering at a temperature of 750°C. for one hour.

The yield point of the steel was $E=60 \text{ kg./mm.}^2$.

This steel was placed in contact with a saturated solution of sulfuric acid and was maintained under flexure. No cracking was noted in 2000 hours.

Example III

Test pieces were obtained in a steel having the following composition by weight:

	Percent
C -----	0.19
Si -----	0.29
Mn -----	0.47
Cr -----	2.22
Mo -----	1.01
V -----	0.23
S -----	0.021
P -----	0.021
Fe -----	Remainder

4

This steel was submitted to the following treatment:

First treatment stage: Austenitization at 980°C. followed by air cooling (one hour).

Second treatment stage: Tempering at a temperature of 725°C. for one hour.

The yield point of the steel was $E=67.1 \text{ kg./mm.}^2$.

The steel was placed in contact with a saturated solution of sulfuric acid and was maintained under flexure. A crack was observed at 320 hours. No other cracks were produced in 3300 hours.

A steel having the same composition was submitted to the following treatment:

First treatment stage: Austenitization at 980°C. followed by air cooling (one half hour).

Second treatment stage: Tempering at a temperature of 725°C. for two hours.

The yield point of this steel was $E=63.2 \text{ kg./mm.}^2$.

This steel was placed in contact with a saturated solution of sulfuric acid and was maintained under flexure. No cracking was observed after 4000 hours.

Example IV

Tubes were made from a steel having the following composition:

	Percent
C -----	0.14
Si -----	0.14
Mn -----	0.45
Cr -----	2.49
Mo -----	0.90
V -----	0.22
S -----	0.011
P -----	0.020
Fe -----	Remainder

These tubes are intended for use in petroleum wells wherein the gases contain a volumetric proportion of 15 to 25% hydrogen sulfide.

The tubes were subjected to the following treatment:

First treatment stage: Austenitization at a temperature of from 1000° to 1050°C. for a period of about 4 minutes in a tunnel furnace. The cooling was effected by means of water at least at the rate specified in Example I.

Second treatment stage: Tempering at a temperature of approximately 750°C. for about one hour.

The tensile properties thus obtained are as follows:

Yield point ----- $E=60 \text{ kg./mm.}^2$.
 Ultimate strength --- $R=69 \text{ kg./mm.}^2$.
 Elongation ----- $A=25\%$ (test pieces made of the steel of the tubes having a useful length equal to four times their diameter).

The structure of the steel is analogous to that indicated in Example I.

Test pieces, made of the metal of the tubes of the present example and given the same treatment, were then subjected to the test described in Example I. No cracks were observed after 3000 hours.

Example V

Test pieces were made from a steel having the following composition by weight:

	Percent
C -----	0.20
Si -----	0.23
Mn -----	0.52
Cr -----	11.5
Mo -----	1.10
V -----	0.30
Ni -----	0.40
S -----	0.015
P -----	0.020
Fe -----	Remainder

This steel is intended for contact with a solution of hydrogen sulfide. The high chromium content of this steel is for the purpose of improving its resistance to generalized corrosion, i.e., to reduce the loss in thickness of parts during service.

The steel was subjected to the following treatment:

First treatment stage: Austenitization at a temperature of approximately 1000° C. for about 15 minutes, followed by cooling with air at least at the rate specified in Example I.

Second treatment stage: Tempering at a temperature of approximately 775° C. for about one hour.

The tensile properties obtained are as follows:

Yield point..... E=61 kg./mm.².
Ultimate strength..... R=82 kg./mm.².
Elongation..... A=25% (the useful length of the test piece being equal to four times its diameter).

The structure of the steel is analogous to that indicated in Example I.

The steel thus treated was tested in the manner described in Example I. No cracks were observed after 3000 hours.

It is to be understood that the examples given above are indicative of only a few specific applications of the invention. The temperatures and the duration of the treatments above indicated may vary within certain limits without departing from the principles underlying the invention.

Insofar as the austenitization temperature is concerned, it should vary only from 975° to 1100° C. As to the tempering temperature, it should vary only in the range between 725° and 800° C.

The choice of the preferred temperatures to be used within these ranges, as well as the duration of the tempering step, must depend upon the yield point to be obtained which lies between 55 and 65 kg./mm.², according to the amount of carbon (see Fig. 3).

Finally, in the preceding examples it was indicated that the cooling could be effected either with air (Examples I, II, III and V) or with water (Example IV). The choice of the cooling medium obviously depends upon the shape and thickness of the structural parts since the cooling must be sufficiently rapid to insure the hardening of the steel.

What is claimed is:

1. A process for manufacturing an alloyed steel element having fine spheroidized carbide particles uniformly distributed in the ferritic matrix capable of stress corrosion cracking resistance in a moist atmosphere charged with hydrogen sulfide including the steps of austenitizing an alloyed steel element having a composition comprising from 0.10 to 0.25% carbon, from 0.10 to 0.50% silicon, from 0.30 to 1.0% manganese, from 1 to 14% chromium, from 0.40 to 1.5% molybdenum, from 0.10 to 0.60% vanadium, from 0 to 1% nickel, and minor quantities of other elements such as sulfur up to 0.030%, phosphorus up to 0.025%, copper up to 0.20%, the remainder being substantially all iron, at a temperature between 975° and 1100° C., cooling the steel at a speed at least equal to 30° C. per minute between 850° and 600° C., and then tempering the steel at a temperature between 725° and 800° C. for a period of time sufficient to produce a yield point between 55 and 65 kg./mm.², according to the amount of carbon.

2. A process as defined in claim 1 wherein the austenitizing treatment is conducted at a temperature between 980° and 1000° C. for a period of about one hour.

3. A process as defined in claim 1 wherein the austenitizing treatment is conducted at a temperature between 1000° and 1050° C. for a period of about 1 to 5 minutes.

4. A process as defined in claim 1 wherein the tempering treatment is conducted at a temperature of approximately and not less than 750° C. for a period of about one hour.

5. A process for manufacturing an alloyed steel element having fine spheroidized carbide particles uniformly distributed in the ferritic matrix capable of stress corrosion cracking resistance in a moist atmosphere charged with hydrogen sulfide including the steps of austenitizing an alloyed steel element having a composition comprising about 0.17% carbon, 0.30% silicon, 0.50% manganese, 2.5% chromium, 1% molybdenum, 0.25% vanadium, 0.2% nickel, 0.02% sulphur and 0.015% phosphorus, the remainder being substantially all iron, at a temperature between 980° and 1000° C. for a period of about one hour, cooling the steel at a speed at least equal to 30° C. per minute between 850° and 600° C., and then tempering the steel at a temperature of approximately but not less than 750° C. for a period of about one hour.

6. A process for manufacturing an alloyed steel tube having fine spheroidized carbide particles uniformly distributed in the ferritic matrix capable of stress corrosion cracking resistance in a moist atmosphere charged with hydrogen sulfide including the steps of austenitizing an alloyed steel tube having a composition comprising about 0.14% carbon, 0.14% silicon, 0.45% manganese, 2.49% chromium, 0.90% molybdenum, 0.22% vanadium, 0.011% sulphur and 0.020% phosphorus, the remainder being substantially all iron, at a temperature between 1000° and 1050° C. for a period of about 1 to 5 minutes, cooling the steel at a speed at least equal to 30° C. per minute between 850° and 600° C., and then tempering the steel at a temperature of approximately but not less than 750° C. for a period of about one hour.

7. A process for manufacturing an alloyed steel element having fine spheroidized carbide particles uniformly distributed on the ferritic matrix capable of stress corrosion cracking resistance in a moist atmosphere charged with hydrogen sulfide including the steps of austenitizing an alloyed steel element having a composition comprising about 0.20% carbon, 0.23% silicon, 0.52% manganese, 11.5% chromium, 1.1% molybdenum, 0.30% vanadium, 0.40% nickel, 0.015% sulphur and 0.020% phosphorus, the remainder being substantially all iron, at a temperature of approximately 1000° C. for a period of about 15 minutes, cooling the steel at a rate at least equal to 30° C. per minute between 850° and 600° C., and then tempering the steel at a temperature of approximately but not less than 775° C. for a period of about one hour.

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