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(54) SYSTEMS COMPRISING CAST IRON AND SULPHURIC ACID

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a system in which sulphuric acid is in contact with cast iron, and is concerned more especially with the reduction of corrosion of cast iron in such systems.

In some chemical processes sulphuric acid is obtained as a waste product which may have a sulphuric acid content of from 70 to 90 per cent and contain, in addition to water, organic compounds, mineral salts, hydrochloric acid, nitric acid, and other impurities. Waste acid of such a composition is frequently regenerated according to the method described by H. Pauling in German Patent Specification No. 299.774 (1915). In this process the waste sulphuric acid is supplied to a stripping column which is mounted on a boiler of gray cast iron serving as distilling kettle. The boiler is fired with gas or mineral oil and is filled with boiling concentrated sulphuric acid which is withdrawn and cooled at the same rate as the waste acid is fed in. The water contained in the waste acid leaves the stripping column in the form of water vapour having a temperature of from 130 to 150°C.

The boilers serving as distilling kettles and their covers are generally made of lamellar gray cast iron of pearlitic texture. Investigations into the structure of the cast iron have shown graphite structures of A 3 to C 3 according to ASTM in the pearlitic texture, and the compositions of 2.9 to 3.5% carbon; 1.6 to 1.9% silicon; 0.2 to 0.6% phosphorus; 0.1 to 0.15% sulphur; 0.35 to 0.65% manganese; 0.05 to 0.2% chromium; 0.04 to 0.08% nickel; 0.07 to 0.1% copper; and less than 0.03% aluminium: the remainder being iron and impurities which are common for cast iron. The Pauling process is described in detail by P. Parrish, Trans. Inst. Chem. Engrs. 19 (1941), 1—24 F. Rumford, Chem. Eng. Materials, London 1954, 57—75 BIOS Final Report No. 243 and FIAT Final Report No. 1187, film K—18.

The corrosion of the boilers made of gray cast iron by boiling concentrated sulphuric acid which occurs in the Pauling process has been examined by E. Maahn (Brit. Corros. J. 1966, vol. 1 page 350).

The corrosion depends on the redox potential of the boiler contents and is intensified by reducing components in the sulphuric acid, for example, organic impurities. In order to reduce the corrosion, nitric acid may be mixed with the sulphuric acid so that, if the process is carried out in a suitable manner, the cast iron in the boiling concentrated sulphuric acid is rendered passive, that is to say, it is covered with a thin layer of iron-(III) salts. In this case the loss due to corrosion is up to 1 cm per year on average.

However, the application of nitric acid as auxiliary agent in the reprocessing of waste sulphuric acid in Pauling plants may lead to a number of difficulties. Thus, for example, if the sulphuric acid contains organic substances which can be nitrated, for instance aromatic amines, the nitrated compounds so formed are sometimes difficult to decompose. Also, nitro compounds of this kind may sometimes represent an operational risk. Some of the added nitric acid may also react with sulphuric acid forming nitrosyl-sulphuric acid, which remains as a stable compound in the hot sulphuric acid. Also the elimination of nitrous gases which are formed in the reaction of nitric acid involves high technical expenditure.

The present invention provides a system which comprises cast iron, sulphuric acid in contact with the cast iron, and one or more noble metals (as hereinafter defined), and/or compound thereof, in contact with the sulphuric acid.

The term "noble metal" is used herein to denote the platinum metals, gold, silver and mercury. Gold and the platinum metals, that is to say, ruthenium, rhodium, palladium, osmium, iridium and platinum are preferred, and especially palladium, platinum and gold.

In a system according to the invention, the noble metal may be present in any form, for example, in its elemental state or in the form of one or more simple or complex compounds thereof. It may also be present in other forms, for example in non-stoichiometric mixtures such as alloys, or in cluster compounds etc. When the noble metal is present in its elemental state, it may be in the form of wire, sheet or chips. Other forms may however also be used, for example shavings, turnings, ribbon or filings.

The system of the present invention has the advantage that the rate of corrosion of the cast iron is considerably reduced as compared to systems in which the noble metal or compound thereof is absent.

The cast iron can be protected in a particularly advantageous manner against corrosion by boiling concentrated sulphuric acid by forming a system according to the invention in which the or each noble metal is in contact with the cast iron, especially when they are in close contact. Close contact may be achieved for example, by wrapping the cast iron with wire of the noble metal or by fastening a wire or sheet of the noble metal on the surface of the gray cast iron. Close contact may also be achieved by other methods, for example by the introduction of chips of noble metal into the cast iron during or following the casting process, or by electrolytic deposition of the noble metal on the surface of gray cast iron.

According to the invention, one or more compounds of the noble metals may be contacted with the sulphuric acid instead of, or in addition to, the elemental metals. The noble metal compounds, for example, the oxides, halides or complex metal acids, may be used in quantities equivalent to from 0.01 to about 50 grammes of noble metal per thousand kilogrammes of sulphuric acid system.

The system of the present invention may reduce corrosion of gray cast iron of a pearlitic as well as of a ferritic texture. The graphite portion of the gray cast iron may be present in a lamellar form or as a modular graphite. Surprisingly however, the corrosion-inhibiting effect of the precious metals is not found in the case of unalloyed carbon-containing steel (steel 1.1740).

The formation of a system according to the invention appears to be particularly advantageous for protecting the cast iron at the zones near the surface of the boiling concentrated sulphuric acid.

In some Pauling boilers, this zone is subject to an intensified corrosion (German Patent Specification Nos. 639.225 and 699.770), which results in a groove having a width of up to 10 cm and forming a ring around the boiler.

According to German Offenlegungsschrift No. 2.330.281, impure dilute sulphuric acid is highly concentrated according to the Pauling method in the first step, and subsequently the concentrated sulphuric acid is distilled in the second step. The distillation vessels made of cast iron which are used for this process may be protected according to the invention against the corrosion by the hot concentrated sulphuric acid. Advantageously, in operating a system according to the invention in a process according to German Offenlegungsschrift No. 2.330.281, the added noble metals are separated again completely and recovered in the second step.

The following Examples illustrate the invention.

EXAMPLES (cf. Table I).

A round flask of a capacity of 1 litre was charged with 1 kg of concentrated, commercial and analytically pure sulphuric acid of about 96% strength. The flask was provided with an air-cooled condenser placed on top and a water-cooled condenser arranged above, and was heated by means of an electric heater. The gray cast iron or steel samples were placed or suspended in the flask, and the acid was maintained at its boiling point for 24 hours. In Examples 1 to 8 the air-cooled condenser and the water-cooled condenser served as reflux condensers. If the water contained in the concentrated sulphuric acid as well as the water formed in the corrosion reaction during the test was to be eliminated continuously, the water-cooled condenser arranged following the air-cooled condenser was designed as a descending condenser as in Example 9 to 15. In Examples 2, 3, 4 and 13, each gray cast iron sample was wrapped with platinum or gold wire (diameter of 0.5 mm). If the noble metals were used in the form of compounds, the compound and concentrated sulphuric acid were introduced into the reaction flask, and the corrosion samples were then added. After termination of the heating, the cast iron and steel samples were removed from the flask, rinsed, powerfully rubbed with a cloth, dried and weighed. The cast iron and steel samples are characterised in Table II.

TABLE I

		Noble metal			Corrosion samples				
Example No.	Material	Type	Form of introduction	Amount mg	Mode of introduction	Wrapping with wire of precious metal	Sample surface cm²	Test duration min.	Conc. of H_2SO_4 at the beginning of test %
1	GG 1 GG 2	— —	— —	— —	inserted inserted	— —	17.5 16.3	1445	95.8
2	GG 2	Au	wire	1904.9	inserted	+	19.1	1470	95.8
3	GG 2	Pt	wire	977.2	inserted	+	18.1	1445	about 96
4	GG 2 GG 2	— Pt	— wire	— 978.4	inserted suspended	— +	17.6 18.3	1460	95.8
5	GG 1 GG 2	Au	$HAuCl_4 \cdot xH_2O$	8.13	inserted inserted	— —	17.5 17.5	1450	95.8
6	GG 1 GG 2	Pt	$PtO_2 \cdot xH_2O$	0.87	inserted inserted	—	17.7 17.8	1445	95.8
7	GG 1 GG 2	Pt	$PtO_2 \cdot xH_2O$	9.28	inserted inserted	—	15.7 16.0	1465	95.8
8	GG 1 GG 2	Pd	PdO	9.01	inserted inserted	—	17.7 17.8	1445	95.5
9	GG 2 steel 1.1740	—	—	—	inserted inserted	—	17.1 23.5	1450	95.8
10	GG 2 steel 1.1740	Pt	$PtO_2 \cdot xH_2O$	7.87	inserted inserted		17.0 23.3	1445	95.8

TABLE I (Continued)

Example No.	Material	Noble metal			Corrosion samples				
		Type	Form of introduction	Amount mg	Mode of introduction	Wrapping with wire of precious metal	Sample surface cm²	Test duration min.	Conc. of H_2SO_4 at the beginning of test %
11	GG 2 GG 3	–	–	–	inserted inserted	–	18.4 32.1	1450	95.5
12	GG 2 GG 3	Pt	$PtO_2 \cdot xH_2O$	8.99	inserted inserted	–	17.8 28.5	1455	95.5
13	GG 2 GG 3	– Pt	– wire	– 2118.6	inserted suspended	– +	29.8 27.8	1445	95.8
14	GG 1 GG 2	–	–	–	inserted inserted	–	16.8 16.3	1445	95.8 (1)
15	GG 2	Au	wire	1904.5	inserted	+	18.2	1450	95.8

(1) with 10 g of starch per kg of concentrated analytically pure H_2SO_4. As starch there was used a soluble analytically pure starch $(C_6H_{10}O_5)_n$. Carbon content of the concentrated sulfuric acid at the end of the test: 0.024 %.

TABLE I (Continued)

Example No.	Distillation of water during the test: H_2SO_4 content distillate %	Distillation of water during the test: H_2SO_4 content in the corrosion mixture at the end of test %	Distillation of water during the test: Amount of distillate ml	Rate of corrosion $\frac{mg}{cm^2 \cdot day}$	Noble metal content of conc. H_2SO_4 of the corrosion mixture parts per million
1	–	–	–	195.1 130.0	
2	–	–	–	8.2	<0.05
3	–	–	–	9.0	
4	–	–	–	27.2 8.6	
5	–	–	–	105.7 57.7	0.1
6	–	–	–	33.5 23.5	0.3
7	–	–	–	9.2 8.7	
8	–	–	–	42.9 56.3	7.8
9	17.3	98.0	25	67.1 20.0	
10	21.8	98.6	33	3.9 449.5	2.4

TABLE I (Continued)

Example No.	Distillation of water during the test			Rate of corrosion	Noble metal content of conc. H_2SO_4 of the corrosion mixture
	H_2SO_4 content distillate	H_2SO_4 content in the corrosion mixture at the end of test	Amount of distillate	$\frac{\text{mg}}{\text{cm}^2 \cdot \text{day}}$	
	%	%	ml		parts per million
11	10.9	98.2	42	89.7 443.9	
12	14.8	98.3	30	4.1 6.2	2.4
13	not determ.	not determ.	28	31.6 4.6	
14	16.8	97.4	30	109.3 78.0	
15	23.4	98.1	45	5.5	0.09

TABLE II

Type of gray cast iron No.	GG 1	GG 2	GG 3
Chemical composition			
% C	3.3	3.3	3.53
% Si	2.4	2.3	2.37
% P	0.63	0.61	0.030
% S	0.15	0.14	0.005
% Mn	0.52	0.47	0.22
% Cr	0.068	0.075	0.046
% Ni	0.043	0.032	0.046
% Cu	0.099	0.056	0.058
% Al	<0.03	<0.03	0.07
% Ti	not determ.	0.048	not determ.
% Mg	not determ.	not determ.	0.040
Type and distribution of graphite acc. to ASTM	lamellar A 4	lamellar D 7	nodular graphite
Fundamental texture	largely pearlitic, some ferrite (spots)	largely pearlitic, some ferrite	largely ferritic, some pearlitic islands

Steel 1.1740 = steel C 60 W 3; *guide analysis* C 0.60%; Si 0.25—0.50%, Mn 0.60—0.80%; P max. 0.035%; S max. 0.035%; measured hardness (HV 10): 221; texture: pearlitic with about 15% of ferrite.

The following values were determined analytically:

C = 0.545%

Si = 0.22 %

WHAT WE CLAIM IS:—

1. A system which comprises cast iron, sulphuric acid in contact with the cast iron, and one or more noble metals (as hereinbefore defined), and/or compounds thereof, in contact with the sulphuric acid.

2. A system as claimed in claim 1, wherein at least one noble metal is present in its elemental state.

3. A system as claimed in claim 2, wherein at least one noble metal is present in the form of wire, sheet or chips.

4. A system as claimed in claim 2 or claim 3, wherein at least one noble metal is present in elemental form and is in contact with the cast iron.

5. A system as claimed in any one of claims 1 to 4, wherein at least one noble metal is present in compound form.

6. A system as claimed in claim 5, wherein the or at least one metal compound is an oxide, halide or complex acid of the noble metal.

7. A system as claimed in claim 5 or claim 6, wherein the quantity of noble metal compound present is equivalent to form 0.01 to 50 grammes of noble metal per thousand kilogrammes of sulphuric acid.

8. A system as claimed in any one of claims 1 to 7, wherein the cast iron and the or each noble metal have been contacted with the sulphuric acid substantially simultaneously.

9. A system as claimed in any one of

claims 1 to 8, wherein at least one noble metal and/or compound thereof is present in the cast iron.

10. A system as claimed in claim 1, wherein at least one noble metal is present as an alloy with the cast iron.

11. A system as claimed in any one of claims 1 to 10, wherein the or each noble metal is one of the following: ruthenium, rhodium, palladium, osmium, iridium, platinum or gold.

12. A system as claimed in claim 11, wherein the or each noble metal is one of the following, palladium, platinum or gold.

13. A system substantially as hereinbefore described in any one of Examples 2 to 8, 10, 12, 13 or 15.

14. A system as claimed in any one of claims 1 to 12, wherein the sulphuric acid is being boiled in a boiler comprising the cast iron.

15. A process for recovering sulphuric acid by distillation in a cast iron boiler, wherein the sulphuric acid is contacted with one or more noble metals (as hereinbefore defined), and/or compounds thereof.

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