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METHOD FOR REDUCING SCALE IN BOILERS

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ABSTRACT OF THE DISCLOSURE

A process for reducing scale in boilers in which a polymer having from 20 to 50% amide groups and from 50 to 80% carboxyl groups is added to the boiler water. This polymer has a molecular weight of from about 20,000 to 100,000. Preferably, the polymer is produced by hydrolyzing polyacrylonitrile.

The present invention relates to the reduction and prevention of scale in steam boilers. More specifically, the invention is directed to the use of particular polymeric materials to eliminate scale in boilers.

If water which is to be boiled in a steam boiler contains any hardness, this hardness tends to deposit as scale on the heat exchanging surfaces of the boiler. The scale reduces the heat transfer across the heat exchanging surfaces so that there is an increased tendency for the metal to overheat. This can and often does lead to rupture of boiler exchange surfaces. Present boiler scale reduction practice is to employ compounds such as tannins, modified lignins, algins and other complex organic compounds to prevent the formation of scale on the metal surfaces. The employment of these compounds has one or more of the following disadvantages: (1) oxidization in the boiler, (2) decomposition on the metal surface with deposition of carbon on the metal and failure due to overheating in high pressure boilers, (3) the requirement of relatively large amounts to inhibit scale, (4) certain types of scale, such as magnesium phosphate, are unaffected by conventional types of organic compounds, and (5) conventional boiler scale inhibitors are highly colored so that steam that is contaminated by carryover cannot be used for food processing or other purposes where color and contamination are factors.

It is an object of the present invention to provide a process which is capable of eliminating the above disadvantages.

Still another object of the invention is to provide a relatively inexpensive means for preventing boiler scale.

Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

In general, the subject invention comprises the discovery that particular hydrolyzed polyacrylonitrile materials are extremely effective in inhibiting boiler scale. The hydrolyzed polyacrylonitrile polymer is usually applied in the form of an aqueous solution, although other polar solvents could be used. It is also possible to apply the product in a dry form. Where an aqueous solution is employed, the solution contains from about 1 to 30% hydrolyzed polyacrylonitrile. The lower limit depends upon economic considerations in that it is not economically feasible to ship and handle too great a quantity of water. The upper limit is determined by the viscosity of the solution. Most often the solution will contain from about 10 to 25% hydrolyzed polyacrylonitrile, and more preferably from 15 to 20% hydrolyzed polyacrylonitrile. The molecular weight of the polymer can vary from about 20,000 to 100,000. Preferably, the molecular weight of the polymer will be from 20,000 to 50,000, and more preferably from 20,000 to 40,000. The polymer is best applied at a dosage level in the range of 1 to 20 p.p.m., and preferably at a dosage level of between 2 and 10 p.p.m. It is essential that the hydrolyzed polyacrylonitrile contain a given amount of carboxylic acid groups and a given amount of NH_2 groups. In general, the polymer will have from 20 to 50% amide groups and from 50 to 80% carboxyl groups.

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The following example illustrates preparation of a typical boiler additive of the present invention.

EXAMPLE 1

This example shows a suitable process for preparing polyacrylonitrile. The ingredients that were used in the process include the following:

Ingredient:	Parts (by weight)
Acrylonitrile	14.7
Water (deionized)	51.0
10% ammonium persulfate solution	6.9
10% sodium bisulfite solution	27.4
Total	100.0

The acrylonitrile and water were mixed together in a flask equipped with an agitator, thermometer, and condenser and warmed to 50° C. The ammonium persulfate solution was added to the mixture and two minutes later the sodium bisulfite solution was added. Initiation of polymerization occurred almost immediately. The temperature, which had dropped to 45° C., was allowed to rise at 1.5–2.0 degrees/min. up to 64° C. with partial cooling. The reaction mixture was then cooled and maintained at 55° C. for 3½ hours. The solution was then heated to 80° C. for one-half hour under slight vacuum to remove traces of unreacted acrylonitrile.

There are several methods that can be used to hydrolyze the polyacrylonitrile. Probably the best method is to hydrolyze the polyacrylonitrile slurry with sodium hydroxide in an aqueous medium. One of the problems involved in this procedure is due to the high viscosity level that is reached during the initial stage of the hydrolysis. In order to avoid this difficulty, the polyacrylonitrile can be added to the hydrolyzing medium over a 50–90 minute period. In an illustrative hydrolysis treatment, 24.4 parts by weight of a 50% NaOH solution was placed in a clean reaction vessel equipped with a stirrer, thermometer, and reflux condenser and heated to 90° C. One hundred (100) parts by weight of a 14.7% polyacrylonitrile slurry in water was then fed continuously to the reaction vessel over a 50 minute period. After the last portion of polyacrylonitrile was added, the reaction was heated at 90–100° C. At regular intervals, samples were withdrawn, cooled rapidly to room temperature, and submitted for evaluation. Optimum properties were obtained with material that was hydrolyzed for 2.5–5.0 hours. Length of hydrolysis is dependent on temperature. Analysis by infrared indicated that the best products were composed of 20–50% amide and 50–80% carboxyl groups. The same is true where the boiler additive is prepared by a copolymerization reaction such as by the copolymerization of acrylic acid and acrylamide.

The mol ratio of caustic to acrylonitrile that is used in the hydrolysis is important in determining the extent and rate of hydrolysis. Table 1 shows the composition of products hydrolyzed for 17 to 19 hours using less than the theoretical amount of sodium hydroxide.

TABLE 1.—EFFECT OF CAUSTIC CONCENTRATION ON HYDROLYSIS OF POLYACRYLONITRILE

	Mols NaOH per mol acrylonitrile	Hydrolysis time, hrs.	Composition		
			CN	$CONH_2$	CO_2H
1	0.3	19	12	30	58
2	0.5	17	3	30	67
3	0.6	17	------	32	68
4	0.7	17	------	32	68
5	0.8	17	------	------	------
6	0.9	17	------	29	71

In producing the product, molecular weights are determined by measuring intrinsic viscosity. The following procedure can be used for this purpose:

Polyacrylonitrile is dissolved in dimethyl formamide at room temperature. Ten (10 mls.) of solution is added by pipette to a Cannon-Ubbelohde viscometer and the time required for a standard volume to pass through the capillary is measured. Concentrations of solution are chosen so that the initial time is greater than 500 sec. The concentration of polyacrylonitrile in DMF is decreased to .67, .50, .40, and .25 times the initial concentration. The time required for these solutions to pass through the capillary is measured. Specific viscosity is calculated according to the following formula:

$$\eta_{sp}=\frac{t_p-t_s}{t_s}$$

where:

ηsp=specific viscosity

t_p=time for polymer solution to pass through capillary

t_s=time for solvent to pass through capillary

Intrinsic viscosity was obtained by graphing

$$\frac{\eta_{sp}}{C} \text{ vs. } C$$

where C= concentration; and extrapolating to 0 concentration.

Molecular weight was calculated from the Staudinger equation:

$$[n]=kM^d$$

where:

k and d are constants.

$[n]$=intrinsic viscosity

M=molecular weight for polyacrylonitrile

$k=2.43 \times 10^{-4}$

$d=0.75$

Determining product composition

Product composition can be determined by infrared analysis by comparison of carboxylate vs. amide lines or by titration with strong acid. Of the two procedures, infrared analysis is more rapid and was used in this work.

Standards wer obtained by polymerizing recrystallized acrylamide and distilled acrylic acid in aqueous solution as homopolymers. The polyacrylic acid was neutralized with CO_2 free sodium hydroxide and then mixtures of known composition were prepared from the sodium polyacrylate and the acrylamide. The mixture was then cast on an Irtran–2 plate and run on the IR–9. The relative heights of the 1575 and 1675 cm.$^{-1}$ peaks were compared at acrylic acid:acrylamide ratios of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 and used to estimate composition of the hydrolyzed polyacrylonitriles.

EXAMPLE 2

In the experiments shown in this illustrative example, boiler scale inhibitors of the subject invention were tested to determine their effectiveness. The tests, test materials, etc., were as follows:

Equipment and materials

The tests were run in a No. 1 inclined tube experimental

boiler with natural thermal circulation. The volume at normal operating level was 0.56 gallon. The water level was automatically controlled by three insulated electrodes which made contact with the boiler water to operate relays which controlled the feed water pump and heating element. Pressure control was by manual adjustment of a needle valve in the condensed steam line. Boiler test specimens were low carbon steel tubes, 1 ½" O.D. x 10" long, closed at one end and flanged at the other. The tubes were bolted in the boiler at an angle of 30° from the horizontal with the closed end down. Heat was applied to the inside and water surrounded the outside. A soft corrugated copper gasket was used to seal the tube in the boiler. The test surface itself was cleaned and polished with No. 3/0 emery paper before each test. Heat was supplied to the test specimen by a 3 kw. resistance heating element within the tube. The heat transfer rate was 30,000 B.t.u. per sq. ft. per hour at the evaporation surface. Evaporation rate was approximately 1 gallon per hour (8.3 lbs. per hour). The blowdown rate was 10% of the feed water input to maintain 10 concentrations of feed water solids in the boiler water. The blowdown water was taken from the boiler about 3" below the water level. Continuous blowdown was simulated by a time clock operated solenoid valve which opens for one to two seconds every five minutes. The flow was restricted by a small orifice.

Procedure

A synthetic feed water for these tests was prepared in 5 gal. lots by adding the following amounts of chemicals to distilled water:

	P.p.m.
$MgCl_2$ (as $CaCO_3$)	10
NaOH	13.2
Na_2CO_3	10
Na_3PO_4	7.3
Na_2SO_3	17

The operating pressure was 800 p.s.i. ±50 p.s.i.

The blowdown rate was adjusted to maintain the boiler water concentration ratio at 10. Chemical analyses of the boiler water made at four hour intervals when operators were on duty. Corrective adjustments were made if the readings were outside the following normal ranges:

	P.p.m.
Hardness	0
P alkalinity	250–280
M alkalinity	285–315
O alkalinity	200–250
Chloride	100–125
Phosphate	25–35
Sulfite	5–10

A special procedure was used for starting the tests in order to eliminate the normal concentration build-up at the start of a test before the blowdown was begun. In the tests alkalinity, phosphate, and sulfite were slugged into the boiler fill to bring these components up to the normal ten concentration level. Two-thirds of the treatment needed to give the ten concentration level was also slugged into the initial boiler fill, which was boiled to remove gases before it is put into the boiler.

The first 5.0 gallons of feed water contained only 10 p.p.m. of $MgCl_2$ hardness and one-third of the normal dosage of treatment. After this first five gallons of feed water had been evaporated, the blowdown was turned on and the remaining feed water for the test was treated with the specified amounts of magnesium chloride, alkalinity, disodium phosphate, and sodium sulfite, and treatment.

All feed water was nitrogen blanketed with a small stream of nitrogen gas to reduce oxygen pick-up.

The tests were operated until the heat had been on for 24 hours. This included about one hour for the boiler to reach its operating pressure of 800 p.s.i.

At the end of the 24 hour period, the heat was shut off and the pressure allowed to drop down without changing the steam valve setting. This permitted evaporation during the cool down period and kept suspended solids from settling out on the tube. When the pressure dropped to 50 p.s.i., the boiler was drained rapidly and the tube removed immediately.

In evaluating the results the amount of deposit on the tube was visually estimated by examination under a stereoscopic microscope and by comparing it to a blank test without treatment. Physical properties of the deposit such as color, hardness and distribution were recorded. Relative density and volume of the deposit was compared to the blank. The tube was graded by recording the relative percent of deposit which had been prevented by the boiler additives of the invention falling within the above recited molecular weight range compared to the blank test without treatment. For example, a tube graded 75% scale prevention has only 1/4 (25%) as much deposit as the blank. A tube graded 90% has only 1/10 (10%) as much deposit as the blank. The range of results is from 0%, no effect, to 100% complete deposit prevention.

The percent scale prevention grading system gives relative rather than absolute values for the amount of deposit on a specific tube, since the amount of deposit on a blank tube for different types of tests may vary widely.

The relative activity values (R.A.) shown in the results indicate the relative performance of the material being tested compared to a standard treatment. The relative activity is the ratio of p.p.m. of standard treating agent to p.p.m. of the sample tested to produce the same scale prevention. As an example, if 5 p.p.m. of sample A gave 70% scale prevention and if 34.6 p.p.m. of the standard treating agent was required to give 70% scale prevention, the R.A. of sample A at 5 p.p.m. was 34.6/5=6.92. This figure is useful in calculating cost-performance figures. It indicates that the cost of sample A can be 6.92 times the cost of the standard test material and still be equal to the standard test material on a cost-performance basis.

TABLE 2

Test No.	p.p.m.	Material	Hydrolyzing agent	Prevention	R.A.
1	1	Hydrolyzed PAN [1] 17% solution		60	23.2
2	2	do		65	14.3
3	5	do		80	9.64
4	5	Hydrolyzed PAN 29% solution		75	8.24
5	5	Hydrolyzed PAN dried		65	5.72
6	5	Hydrolyzed PAN	$NaOH-H_2O_2$	80	9.64
7	5	do	$NaOH-H_2O_2-NH_4OH$	70	6.92
8	5	do	$NaOH-NH_4OH$	70	6.92
9	5	do	$NaOH-H_2O_2$	75	8.24
10	5	do	$NaOH-1/2\ H_2O_2$	70	6.92
11	5	Hydrolyze acrylonitrile then polymerize		75	8.24

[1] Polyacrylonitrile.

Tests 1 to 5 were carried out utilizing a hydrolyzed polyacrylonitrile having a carboxylic acid to amide group ratio of 70:30. This material was extremely effective as a boiler scale inhibitor. As is apparent from the relative activity value, this is unusually active even at low concentration levels. Tests 6 to 10 show that a variety of hydrolyzing agents can be employed in preparing the treating agent. Test 11 demonstrates that effective scale preventing polymers may also be made by monomer hydrolysis of acrylonitrile followed by polymerization of the resulted product.

As was explained above, the prevention of magnesium phosphate scale in boilers presents unusual problems. The subject inhibitors, however, are highly effective in preventing the deposit of this type of scale. As is apparent from the above tests the subject polymers give excellent results at low concentration levels even when magnesium and phosphate ions are present. A number of prior art boiler scale preventative materials demonstrated little or no activity in inhibiting formation of magnesium phosphate scale when tested using the above test procedure. For this reason the use of the inhibitors is economical as is evident from the relative active (R.A.) values set out in Table 2.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for reducing magnesium phosphate scale in boilers using scale forming boiler feed water containing magnesium and phosphate ions which comprises: adding to said boiler water a quantity of hydrolyzed polyacrylonitrile, said polyacrylonitrile having from 20 to 50% amide groups and from 50 to 80% carboxyl groups, and having a molecular weight of from about 5,000 to 100,000, said quantity being sufficient to provide a dosage level of 1 to 20 p.p.m. of hydrolyzed polyacrylonitrile.

2. A process for reducing magnesium phosphate scale in boilers using scale forming boiler feed water containing magnesium and phosphate ions which comprises: adding to said boiler water a quantity of hydrolyzed polyacrylonitrile, said polyacrylonitrile having from 20 to 50% amide groups and from 50 to 80% carboxyl groups, and having a molecular weight of from about 20,000 to 100,000, said quantity being sufficient to provide a dosage level of 2 to 10 p.p.m. of hydrolyzed polyacrylonitrile.

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