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REDUCED FOULING OF STEAM TURBINES BY TREATMENT WITH SULFUR CONTAINING COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

A method of eliminating, reducing, or inhibiting the fouling of steam turbines and in particular, the controlling of fouling which is due to the presence of contaminants in the steam by dispersing in the steam employed to operate a turbine between one to fifty parts by weight of a sulphur compound selected from the group consisting of sodium acid sulphite, ethylene sulphite, sodium bisulphate, sodium sulfoxylated formaldehyde, sodium formaldehyde bisulfite and morpholine sulphate for each part by weight of the contaminant contained in the steam.

BACKGROUND OF THE INVENTION

The fouling of steam turbines, while various attributed to a number of different causes and phenomena, is a real and aggravated problem. Such fouling generally affects the turbine, and particularly the turbine blades, to restrict the passage of steam and consequently impair the efficiency of operation of the turbine unit. In addition, accumulated fouling deposits may increase the work load to the extent that damage to, or failure of, the thrust bearings is experienced.

It is generally recognized that most turbine deposits comprise a combination of water soluble materials such as sodium phosphates, carbonates, and sulfates, and water insoluble silicates, which are entrained in the boiler water and/or steam and subsequently deposited in the turbine. As a consequence of this melange of compounds of conflicting chemical and solubility characteristics, previous attempts to cope with turbine fouling have involved inefficient and generally unsatisfactory techniques. Conventional methods have employed the removal of the water soluble constituents by means of mere washing, and the caustic or alkaline leaching of the water insoluble silicates. In any event, such means of controlling turbine fouling have entailed turbine operation at reduced efficiencies, as well as the necessity for frequent shut-downs for the purpose of removing fouling deposits.

It is an object of the present invention to provide methods for the treatment, removal and prevention of further formation of turbine deposites, without necessity for frequent shut-downs and cleanings.

A further object is the provision of compositions for the treatment of the atmosphere of steam turbines during turbine operation, which eliminate, inhibit or reduce the formation of deposits upon the surfaces of the turbine.

The foregoing objects are achieved by means of the addition of certain organic and inorganic sulfur containing compounds to the steam which is employed in the turbine. The sulfur compounds employed as turbine antifoulants in the practice of the invention are:

Sodium acid sulfite	$NaHSO_3$.
Ethylene sulfite	$CH_2=CHSO_3$.
Sodium bisulfate	$NaHSO_4$.
Sodium sulfoxylated formaldehyde	$HOCH_2SO_2Na$.
Sodium formaldehyde bisulfite	$HOCH_2SO_3Na$.
Morpholine sulfate	$C_4H_8ONH \cdot H_2SO_4$.

While the precise mechanism which renders these compounds operative in the practice of the invention has not been defined, it is conceivable that in the superheated steam environment of the turbine, these compositions are converted to SO_2, sulfuric or sulfurous acid, or hydrogen sulfide, or admixtures thereof, and such conversion products accomplish, or contribute to, the achievement of the inventive goals, i.e., the elimination, preclusion or curtailment of fouling deposits in the turbine. Irrespective of the underlying theory, and as is demonstrated by subsequent data, these treating compounds do bring about the achievent of the forementioned inventive goals.

In the practice of the invention, the above compounds are added to the steam which is supplied to the turbine. In a preferred practice, the treating materials are injected into the superheated steam line on the inlet or upstream side of the turbine. However, the treatments may be added to the steam at any point between the manufacture of the steam and its introduction to the turbine, including direct feed to the turbine. Consequently, if the steam system is divided or sectionalized all of the steam need not be treated and treatment may be limited to that steam which is supplied to the turbine or turbines. Since the treated system is under pressure, the introduction or injection of the treating materials must naturally be achieved at a pressure greater than that which is present within the system treated. Such injection is common in the treatment of high pressure systems and may be achieved by a high pressure piston pump which feeds to an injection or dispersion quill positioned in the high pressure line or chamber to which feeding is to be accomplished. The inlet aperture of the quill is preferably located within the atmosphere to be treated and not in proximity to the line or chamber wall which is pierced by the quill. In those systems which possess a single header supplying the superheater through a distribution header within the superheater, the treating material may be added to the saturated steam as it leaves the boiler drum and prior to its introduction to the superheater system.

However, it should be noted that the treating materials may not be added to the boiler water or boiler feed water. In the first instance, treatment of the boiler or feed water would be grossly uneconomical since a portion of the treating materials would be removed and discarded during the necessary blowdown of concentrated boiler water containing high solids. Secondly, if the treatment is added to the boiler or feed water, its transfer to the steam would be dependent upon carry-over. Carry-over is an undesirable phenomenon in which boiler water and its solids content is transferred to the steam. Positive steps to prevent such occurrence are taken in the form of chemical treatment of the boiler water, e.g., the addition of antifoam agents, and mechanical means, e.g., the installation of baffles. Accordingly, if the inventive treatments were added to the boiler water, their transfer to the turbine section would be dependent upon carry-over which would also operate to increase the contamination of the turbine by the deposit forming materials which is contrary to the inventive purpose, i.e., the elimination or reduction of turbine fouling.

Experience and testing have indicated that the inventive goals are frequently realized when the inventive treating materials are added to the steam at a level of less than one part by weight for each one million parts of steam flow. However, proper treatment should be based upon the total quantity of contaminant salts contained by the steam. Preferably between 1 to 50 parts by weight of the treating material are employed for each part by weight of contaminating salts. It should be noted that the term "contaminating salts" is employed to connote those con-

taminants which are present in the boiler system as the result of naturally occurring contaminants in the boiling water supply, other chemical treatments employed within the boiler system, materials derived from the decomposition of the boiler components, e.g., iron and copper oxides, and intermediate contaminants formed by the decomposition of basic contaminants, e.g., sodium carbonate → sodium oxide. Such contaminants may be generally defined as the salts, oxides and hydroxides of sodium, silica, iron and copper such as silicon dioxide, iron oxide, copper oxide, sodium oxide, sodium chloride, sodium hydroxide, sodium carbonate, sodium phosphate, sodium silicate, sodium sulfate, sodium sulfite, sodium nitrate, etc. although the exact nature and ratio of these contaminants is obviously dependent upon the contaminants present in the boiler feed water, chemicals added to the boiler system, etc. The precise nature and quantity of such salts may be readily determined by tests such as sodium studies which establish steam purity. Since the contaminants in the steam are normally present at levels of less than 1 p.p.m., and usually less than 0.1 p.p.m., the quantity of treatment required will normally not exceed 50 p.p.m. and will usually be between 0.1 to 1.0 p.p.m. of the treating materials. However, it should be noted that higher treatment levels may be employed without appreciably increasing the benefits provided by the invention. In this regard, excessively high treatment levels may not only remove fouling deposits but may result in corrosive attack upon the metal component of the turbine. The level at which such attack occurs varies from case to case since the dissolution of the fouling deposits is preferential to corrosion and treating materials may be completely dissipated in the former if adequate deposits are available. In some cases, minor or controlled corrosion of the turbine may even be accepted in preference to turbine shut-down for the purpose of removing fouling deposits.

An additional, although secondary aspect of the present invention, concerns the control of corrosion. Specifically, morpholine sulfate, prepared by neutralizing morpholine with sulfuric acid, may be employed to provide a treating material which functions simultaneously as an anti-foulant and a corrosion inhibitor. Morpholine is released within the turbine and volatilized by the steam. It then serves to neutralize corrosive agents such as carbonic acid, SO_2, etc., by combining with them to neutralize their acidity.

Other corrosion inhibitors and neutralizing agents, e.g., ammonia, cyclohexylamine, etc., may also be combined with the inventive treatments to reduce or control corrosive factors within the turbine.

For ease of feeding, relatively dilute aqueous solutions, e.g., less than 50% are preferred. However, concentrated or pure treatments may be employed and solvents, diluents and carriers other than water are suitable although less desirable. It should also be noted that a number of the inventive treating materials are corrosive and that corrosion resistant mix and feed tanks, pumps and injection lines are recommended.

The efficacy of the inventive treatments has been thoroughly explored and established in the treatment of duplicate two-stage, noncondensing turbines, hereafter referred to as turbines A and B, having a normal speed of 3,600 r.p.m., and a steam rate of 30,000–33,000 pounds per hour. Steam conditions of these turbines are represented by inlet steam at 600 p.s.i.g. at a total temperature of approximately 700° F., with exit steam at 200 p.s.i.g. and an approximate steam temperature of 440° F. These conditions represent inlet steam at 200 degrees superheat and outlet steam at 50 degrees superheat.

In considering the following results, which are based primarily upon the operating efficiency of the turbines, it should be noted that prior to the initiation of the inventive treatment the shut-down of each turbine for the purpose of removing fouling deposits was required every 9 or 10 days. During the inventive treatments the turbines were operated for periods in excess of 30 days without necessity for shut-down, and in several instances shut-downs after 45 days or more were found to be unnecessary when the turbines were opened and examined.

As a portion of this study, turbines A and B were both operated for 10 day periods without treatment to determine what degree of impairment of their operating efficiency was experienced. In all of the described tests operating efficiency was determined by measuring the maximum number of revolutions which could be obtained from the turbine at noon on each test day. The results of these control tests are set forth in Table 1, below:

TABLE 1

Turbine	Maximum Revolutions per Minute		Percent Decrease in Operating Efficiency	Daily Decrease in Operating Efficiency (total percent decrease/ No. of days)
	1st Day	10th Day		
A	3,900	3,475	10.9	1.09
B	3,850	3,500	9.1	.91

In order to establish the general suitability of the inventive treatments, each of the turbines was also treated with a number of the inventive treatments for a period of 10 days. The results, as contrasted with the results realized with the control tests as shown by Table 1, are set forth in Table 2 below:

TABLE 2

Turbine	Active Ingredient of the Treatment	Percent by Weight of Active Ingredients Contained by Treatment	Quantity of Treatment Employed (p.p.m.)	Quantity of Active Ingredient Employed (p.p.m.)	Duration of Test (Days)	Maximum r.p.m.'s Yielded by Turbine		Percent Decrease in Operating Efficiency	Daily Decrease in Operating Efficiency (Percent Decrease/ Number of Days)	Percentage Improvement
						1st Day of Test	Final Day of Test			
A	None	0	0	0	10	3,900	3,475	10.9	1.09	
A	Ethylene Sulfite	2	2.5	0.05	10	3,800	3,750	1.3	0.13	88
A	do	2	10	0.2	10	3,800	3,800	0	0	100
A	do	2	10	0.2	10	3,850	3,800	1.3	0.13	88
A	Sodium Acid Sulfite	100	0.3	0.3	10	3,700	3,650	1.3	0.13	88
A	do	30	2	0.6	10	3,950	3,900	1.3	0.13	88
A	Sodium Formaldehyde Bisulfite.	2	22.5	0.45	10	3,750	3,750	0	0	100
A	do	30	2	0.6	10	3,700	3,650	1.3	0.13	88
A	do	30	3	0.9	10	3,775	3,700	2	0.2	81.6
B	None	0	0	0	10	3,850	3,500	9.1	0.91	
B	Sodium Sulfoxylated Formaldehyde.	2	22.5	0.45	10	3,700	3,700	0	0	100
B	Sodium Bisulfate	2	15	0.3	10	3,755	3,750	0	0	100
B	Sodium Acid Sulfite	30	3	0.9	10	3,850	3,850	0	0	100

As demonstrated by the above data, the inventive treatments have consistently reduced the gradual decrease in operating efficiency experienced in the absence of an anti-fouling treatment, by between 81.6–100%. However, this reduction in efficiency is only a portion of the picture. Specifically, the basic objective of the invention is an increase in the continuous operation time of the turbine due to the reduced frequency of the necessity for turbine cleaning. Since the reduction in the efficiency of the operation of turbines A and B which is shown by Table 1,

was such as to require the cleaning of the turbines, these 10 day tests were employed as controls in the study discussed hereafter. Specifically, turbines A and B were treated with the inventive treatments and continuously operated until the degree of reduced efficiency experienced in the control tests was achieved, i.e., 10.9% in respect to turbine A and 9.1% in respect to turbine B. The results of this study are set forth in Table 3, below:

TABLE 3

Turbine	Chemical Treatment	Quantity of Chemical Employed (p.p.m.)	Percentage Decrease Operating Efficiency	Period of Continuous Operation of Turbine (Days)	Percentage Increase in Period of Continuous Operation	Remarks
A	None	0	10.9	10		Control.
A	Ethylene sulfite	0.02	10.4	34	340	Test terminated for other reasons.
A	Sodium acid sulfite	0.30	10.9	58	580	
A	Sodium formaldehyde bisulfite	0.45	2.7	19	190	
A	Sodium acid sulfite	0.6	7.8	46	460	
B	None	0	9.1	10		Control.
B	Sodium sulfoxylated formaldehyde	0.45	4.7	28	280	Test terminatef for other reasons.
B	Sodium bisulfate	0.3	7	24	240	Do.
B	Sodium acid sulfite	0.6	5.3	39	390	Do.

It must be noted that all but one of the trials were terminated prior to their completion due to reasons other than the necessity for removing fouling deposits from the turbine. However, in the one test which was completed, the continuous operation of the turbine was extended from 10 to 58 days to permit the operation of the turbine to be extended by nearly 6 times the previous performance. Curves of the decrease in performance for each of the other tests also indicate that continuous operation could have been extended for comparable periods if the tests had been continued.

It should also be noted that while corrosion inhibition studies in respect to morpholine sulfate have not been completed due to the negligible corrosion rate experienced with the inventive compounds, the anti-fouling effect of this compound has been established. In addition, the release of morpholine under the conditions experienced in a steam turbine is demonstrable, and the efficacy of morpholine in providing a neutralizing effect and inhibiting corrosion in steam environments has previously been established.

Another noteworthy aspect of the invention is the minute quantity of treating material required for the elimination or curtailment of fouling. For example, in the treatment of turbine B with sodium acid sulfite for a 58 day period of continuous operation, approximately 41,760,000 pounds of steam were treated and employed in producing over 300,000,000 revolutions of the turbine. This substantial output involved the utilization of only approximately 125 pounds of the chemical employed to treat the turbine. Viewed somewhat differently, the utilization of 125 pounds of chemical treatment, fed automatically and with no labor requirements other than the infrequent replenishing of the chemical supply, permitted the avoidance of at least 5 shut-downs for the cleaning of the turbine which would have been required in the absence of the inventive treatment. The loss of operating time entailed in 5 cleaning operations as well as the expense of labor and materials for such cleaning, are consequently avoided by means of the utilization of a small quantity of a relatively inexpensive chemical.

It is apparent that the applicant has provided methods and materials which provide an extensive improvement in greatly extending the period in which a steam turbine may be operated between clean-ups, reducing the decrease in the efficiency of operation of steam turbines which is normally caused by the formulation of fouling deposits within the turbine, improving the economic operation of steam turbines by reducing the time lost during clean-ups and the labor and material involved in such cleaning operations, and providing highly efficient and economical methods for the achievement of such improvements.

I claim:

1. A method for reducing the fouling of a steam turbine by contaminants entrained in the steam employed to operate the turbine, comprising dispersing within said steam between 1 to 50 parts by weight of a sulfur compound selected from the group consisting of sodium acid sulfite, ethylene sulfite, sodium bisulfate, sodium sulfoxylated formaldehyde, sodium formaldehyde bisulfite and morpholine sulfate, for each part by weight of said contaminants.

2. A method as claimed by claim 1 in which sulfur compound is dispersed within the portion of said steam contained by said turbine.

3. A method as claimed by claim 1 in which said sulfur compound is dispersed within said steam prior to the introduction of said steam to said turbine.

4. A method as claimed by claim 1 in which a corrosion inhibitor is also dispersed within said steam.

5. A method as claimed by claim 4 in which said corrosion inhibitor is selected from the group consisting of morpholine, cyclohexylamine and ammonia.

6. A method as claimed by claim 4 in which said corrosion inhibitor is morpholine.

7. A method as claimed by claim 1 in which said sulfur compound is dispersed in said steam as a dilute dispersion of said sulfur compound.

8. A method as claimed by claim 7 in which said dilute dispersion is an aqueous solution of said sulfur compound.

9. A method as claimed by claim 1 in which said sulfur compound is sodium acid sulfite.

10. A method as claimed by claim 8 in which said sulfur compound is sodium acid sulphite.

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