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THE TAR MOISTURE PROBLEM

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THE TAR MOISTURE PROBLEM

D-2-046-000

INTERLAKE STEEL CORPORATION

RESEARCH DEPARTMENT

V. D. Beaucaire

February 28, 1966

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THE TAR MOISTURE PROBLEM

SUMMARY

The increase in the water content of the tar produced at the Chicago Plant has been investigated both statistically and chemically. While a multiple regression analysis does not permit the pinpointing of any one factor as the definite cause of the problem, laboratory tests have been somewhat more successful. A commercial demulsifying agent, "Tret-O-Lite" R-72, has successfully dehydrated the tar on both laboratory and plant-test scales.

INTRODUCTION

In 1965, Interlake commenced the use of Illinois coal in the coke ovens of the Chicago Plant. Starting in Feburary of that year, coal mixes of various compositions were charged to the ovens in an effort to determine the optimum balance between coke quality and cost of materials. The quality of coke was maintained at a satisfactory level, but a problem related to the change in coal charge did appear. The tar produced as a by-product of the coking operation took a sharp increase in water content, the system being a water-in-oil type emulsion.

Previous to the use of Illinois coal, tar moisture had been no problem. In the years 1963 and 1964, for example, the water content remained below the target level of two per cent. In 1965, however, the moisture concentration in the production tar rose sharply, hitting a peak of 9.4 per cent in the month of September. Efforts to improve the quality of this by-product were clearly in order.

POSSIBLE SOLUTION

There are seven basic methods used for dehydrating commercial scale water-in-oil emulsions. These procedures are employed extensively for breaking oil field emulsions. They are: (1) settling, (2) heating or distilling at atmospheric pressure, (3) heating or distilling at elevated pressures, (4) electrical dehydration, (5) use of chemicals, (6) centrifuging, and (7) filtration. Of the seven possibilities, six were quickly labeled undesirable or unworkable for the problem at hand:

(A) Insufficient separation occurred by settling, even after the tar emulsion was left in storage tanks for long periods of time.

(B) Distillation at atmospheric or elevated pressures would definitely remove the water, but the operation would be costly and time consuming.

(C) Electrical dehydration would not only require the installation of special equipment, but results obtained with this method have been variable.

(D) Centrifuging is possible, and the equipment is already available at the coke plant, but these dehydrators are expensive to operate and require constant maintenance.

(E) Filtration of a viscous material like tar is not practical.

This process of elimination left only the use of chemicals (water included) as a means of attacking the problem.

ACTION TAKEN

The "use of chemicals" was divided into two parts: (1) commercial demulsifying agents, and (2) water and aqueous solutions. The Tretolite Division of the Petrolite Corporation, the largest manufacturer of commercial demulsifying agents, was contacted, and a five gallon sample of tar was sent to their laboratory for examination. Subsequently, samples of demulsifiers were requested from Nalco Chemical Company and Universal Chemicals Corporation.

In addition to making the above contacts, investigative work was conducted in the laboratory of Interlake's Chicago furnace plant. A large number of tar samples were shaken or electrically blended with approximately equal volumes of water and various aqueous solutions. The use of water had a twofold purpose: (1) it would give the effect of "infinitely" diluting the flushing liquor in the system, and (2) water is the dispersed phase in the tar mixture, and sometimes agitating with an excess of the dispersed phase breaks emulsions.

Various aqueous solutions were mixed with the emulsion. In addition to providing an excess of the dispersed phase, such treatment would alter the ionic environment of the system. This latter effect is sometimes beneficial if it tends to "reverse" an emulsion (the dispersed phase becomes the dispersing medium and vice versa). If such treatment proved to be effective in the lab, it might be possible to alter the composition of the flushing liquor to some extent and produce the same effect in the coke plant.

The tests involving water and aqueous solutions were conducted as follows:

(1) Approximately equal volumes of the tar sample and aqueous solution (or water) were heated to 180 F. in separate flasks.

(2) Both phases were poured into an electric blender and were vigorously mixed for one minute.

(3) The mixture was poured into a separatory funnel and the funnel was left at 170 F. for about 18 hours.

(4) The lower organic phase was removed and analyzed for water content.

Most of the treatments removed some of the water, a few had adverse effects. Table I summarizes the results of these tests.

TABLE I. AQUEOUS TREATMENT OF TAR EMULSION

Solution	Effect on Emulsion
Water	Reduced water content
Ammonium chloride (15g/l, 50g/l)	Reduced water content
Sodium chloride (25 g/l)	Reduced water content
Ammonium sulfate (15g/l, 50g/l)	Increased water content
Phenol (0.1 g/l, 1 g/l)	Reduced water content
Hydrochloric acid (3-20g/l)	Increased water content
Sodium hydroxide (0.4-4g/l)	Reduced water content
Ammonium hydroxide (4g/l)	Reduced water content
Calcium oxide (1 g/l)	Reduced water content
Flushing liquor	Reduced water content

Since none of the solutions showed a marked improvement over water treatment, and since the flushing liquor in the coke plant is diluted to capacity as a matter of course, no recommendations on altering the flushing liquor could be made from the results of these tests.

Approximately two weeks after the sample of tar emulsion had been sent to Tretolite, a letter was received from that company stating their laboratory had found a demulsifying agent that had effectively separated the water. A five gallon sample of this chemical, "Tret-O-Lite" R-72, was ordered, and tests were performed at Interlake's laboratory.

Nalco's demulsifiers were examined simultaneously, but these latter tests were not as extensive as those with the Tretolite additive since success by Tretolite had already been claimed, and since preliminary tests with Nalco's materials did not show them to be superior to the other product. * The results of the tests with "Tret-O-Lite" R-72 were favorable to the additive, so it was decided to give the chemical a trial in the coke plant.

By December, 1965, the No. 14 storage tank in the coke plant had accumulated about 500,000 gallons of tar that held an estimated 25 per cent water. This material was so viscous that it caused trouble with the centrifuges, so it was decided to see the effect "Tret-O-Lite" R-72 would have on it. This tar was pumped in 40,000 gallon quantities to the No. 8 tank, 20 gallons (a 2000:1 ratio) of Tretolite's agent being added during transfer. After circulating in the No. 8 tank for 16 hours with air purging, the emulsion was left to stand at about 190 F. The additive proved to be effective; typical results are recorded below:

Time	Water Concentration (%)
Start	35+
4 days	5.0
6 days	2.7

More than half of the tar in the No. 14 tank had been treated in this manner before Koppers Company requested the treatment be stopped. The Koppers Company had in their history some unhappy experiences with additive-treated tar, and they desired to run laboratory tests on "Tret-O-Lite" R-72 before Interlake began using the material as standard procedure.

A statistical analysis of the tar production system is presented in Appendix A.

* The samples from Universal Chemicals Corporation, designed to reduce very high moisture content emulsions to the 10 per cent water level, were lost in the mail. By the time new samples had been received, laboratory tests had been concluded.

THE FUTURE

Mr. Robert Meyer, area representative of the Tretolite Division, has assured Interlake that the additive in question contains no material that might be troublesome to Koppers' operations, but further use of the chemical will not be made until a statement from Koppers Company is received.

On the basis of these tests, "Tret-O-Lite" R-72 appears to be the solution to the tar moisture problem. Should Koppers Company find no fault with the additive, as is expected, the next step would be the installation of an injection system in the tar production line at the coke plant. * The establishment of adequate flow control, thorough mixing, and a proper settling time should insure the solution to Interlake's tar moisture problem.

* On February 28, 1966, Koppers Company notified Interlake that the use of "Tret-O-Lite" R-72 in the batch method is permissible. This decision is concerned only with the treatment of tar in No. 14 tank, however; Interlake must again contact Koppers Company before using the demulsifying agent in the production system.

V. D. Beaucaire

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APPENDIX A

STATISTICAL ANALYSIS OF THE TAR PRODUCTION SYSTEM

STATISTICAL ANALYSIS OF THE TAR PRODUCTION SYSTEM

In addition to the laboratory and plant tests, a multiple regression analysis was performed using the IBM 1410 Data Processing System at the Riverdale Plant. The idea behind this statistical analysis was to determine if the water content of the tar could be correlated with either coal composition or some phase of the coke plant operation. Separate runs were made for both one year (1965) and three year (1963-1965) periods using the data contained in the monthly reports of Interlake's laboratory at the Chicago furnace plant.

For reference, the simple correlation coefficient between a factor and itself is +1.00. The closer the correlation coefficient is to unity (plus or minus), the better the correlation. Table A-I lists the results.

TABLE A-I. Simple correlation Coefficients for Water in Production Tar

Per Cent Water With:	Three Years	One Year
Gallons of tar produced	+0.33	-0.27
Free ammonia in flushing liquor	-0.77	-0.74
Fixed ammonia in flushing liquor	+0.80	+0.50
Total ammonia in flushing liquor	+0.70	+0.37
Ammonium chloride in tar	+0.82	+0.32
Tar acids	-0.56	-0.47
Quinoline insoluble material	+0.69	+0.68
Carbon disulfide insoluble material	+0.69	+0.54
"X" *	-0.70	-0.47
Specific gravity of tar	+0.64	+0.57
Viscosity of tar	+0.43	+0.34
Coal moisture	+0.85	+0.52
Coal volatile matter	+0.12	+0.36
Coal fixed carbon	-0.05	-0.44
Coal ash	+0.04	+0.48
Coal Sulfur	-0.14	+0.33

* "X" = 100 - [% tar acids + % tar bases + % naphthalene + % water + % carbon disulfide insoluble material]

The two factors that maintain fairly good correlation for both the one and three year periods are free ammonia content of the flushing liquor and the amount of quinoline insoluble material in the tar. The free ammonia relationship to the water content of tar is inverse; that of quinoline insoluble material (carbon particles) is direct. Actually, the free ammonia content of the flushing liquor did decline in 1965, dropping to 1.00 grams per liter from a 1963-1964 average of 1.48 grams per liter. In addition, the amount of quinoline insoluble material in the tar rose to 2.61 per cent from a 1963-1964 average of 2.00 per cent. This latter factor is probably a result of the higher oven temperatures necessary to produce 16-hour coke. It is interesting to note, also, that carbon black can stabilize water-in-oil emulsions.*

* Weiser, H. B., Colloid Chemistry, John Wiley and Sons, Inc., New York, 1939, Page 307.

GAB-6

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INTEROFFICE CORRESPONDENCE

Copies to:

Date: November 8, 1965

J. Duncan
R. Nagan
T. Barnes
R & D File

To: Mr. N. H. Keyser

From: V. Beaucaire

Subject: REMOVAL OF WATER FROM TAR

Reference:

The use of Illinois coal in the coking process has resulted in the production of tar that is high in both water and ammonium chloride content. In an effort to reduce the concentrations of these undesirable components, a series of trials involving water washing, centrifuging, and "Tret-O-Lite" Demulsifier R-72 was run. The tar sample was obtained from the coke plant on November 1, the coal blend being 40 per cent Old Ben, 40 per cent Princess Sewell, and 20 per cent Olga. The temperature of the test series was maintained at 180° F.

The results of the investigation are recorded in Table 1.

TABLE 1. Water and Ammonium Chloride Concentrations of Treated Tar

	Treatment			Results	
Trial	Water Wash[a,c]	R-72[b,c]	Centrifuge[d]	%Water	NH_4Cl[e] (g./100,000 g.tar)
1(Base)	No	No	No	3.5	75.5
2	No	No	Yes	1.7	33.4
3	Yes	No	No	1.9	6.8
4	Yes^*_1	No	Yes_2	1.0	5.4
5	Yes_1	Yes_2	No	1.4	7.6
6	Yes_1	Yes_2	Yes_3	1.1	4.8

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	Treatment			Results	
Trial	Water Wash[a,c]	R-72[b,c]	Centrifuge[d]	%Water	NH_4Cl[e] (g./100,000 g.tar)
7	No	Yes	No	2.0	57.8
8	No	Yes_1	Yes_2	1.2	30.6
9f	Yes_1	Yes_1	No	2.2	7.4
10	Yes_1	Yes_1	Yes_2	0.9	2.9
11	Yes_1	Yes_1	No	1.6	4.3
12	Yes_1	Yes_1	Yes_2	0.9	2.2

a. Mixed one minute on low speed in the blender; 300 ml. tar plus 200 ml. water.

b. Mixed three minutes on high speed in the blender at 22 volts, the concentration being 1:2000.

c. After treatment, the mixtures were left standing at 180°F. for 5-6 hours.

d. Centrifuged on setting 7 (high) for two minutes.

e. The four high values are accurate within a few per cent; the lower values are only approximate (compare duplicate runs 10 and 12). * Subscripts indicate order of treatment.

f. On runs 9-12, the R-72 was first blended, then the water was added and mixed before standing at 180°F. Water was evident after overnight standing at room temperature. On run 11, this water was removed before the water and chloride tests were made.

While treatments with water, "Tret-O-Lite" Demulsifier R-72, and the centrifuge individually led to approximately equal water contents (1.7-2.0 per cent), water washing was by far more effective than the other methods in lowering the ammonium chloride concentration. In addition, combinations of the three procedures led to water contents ranging from 0.9-2.2 per cent, and ammonium chloride concentrations between 2.2 and 30.6 grams per 100,000 grams of tar.

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To confirm the belief that the ammonium chloride is present in the aqueous portion of the tar emulsion, the concentrations of this salt per one per cent water were calculated for the four trials involving unwashed tar. The results, recorded in Table 2, show approximately equal concentrations and indicate that the salt is contained in the water.

TABLE 2. Ammonium Chloride Content Per One Per Cent Water

Trial	% H_2O	g.NH_4Cl/100,000 g.tar	g.NH_4Cl/100,000 g.tar per 1% H_2O
1	3.5	75.5	21.7
2	1.7	33.4	19.7
7	2.0	57.8	28.9
8	1.2	30.6	25.4

This trial series will be repeated on a tar sample that contains a higher initial water concentration (ca. 7-10 per cent) when such a sample is available. In addition, another demulsifier, Fatchemco T.E.B. has been ordered from the Universal Chemical Co. The efficiency of this chemical in solving the problem will be determined upon its reception.

VB:vw

Interlake
STEEL CORPORATION

INTEROFFICE CORRESPONDENCE

Date: March 21, 1966

Copies to:
E. F. Lowe
R. A. Nagan
D. Garthus
V. Beaucaire
R&D Files

To: J. W. Duncan

From: N. H. Keyser

Subject: Control of Water Content in Tar from Illinois Coal.

Reference:

We have reached a logical stopping point in our investigation of methods to control the moisture content of the tar from Illinois Coal. Mr. Beaucaire's report on the investigation is attached.

An understanding of the problem and its solution was complicated by more than one variable at play. There appears to be at least two important factors, one in the flushing liquor and one in the tar, which contribute to a high moisture content in the tar.

(1) A decrease in ammonia content of the liquor is reflected in high moisture contents of the tar. Acidifying the liquor in the laboratory actually resulted in more complete emulsification in (higher water contents).

(2) A high carbon content of the tar, as measured by the quinoline insoluble fraction, also contributes to retention of higher moisture contents.

(3) Other factors, such as ammonium chloride content of the liquor, which are believed to influence tar moisture were more evasive and direct relationships could not be proven.

Diluting the flushing liquor with as much water as could be handled from the disposal standpoint turned out to be an effective measure to control moisture contents to satisfactory levels. An emulsion breaking agent with the trade name Tretolite 72 was effective for removing water from batches of tar in the storage tanks.

We plan no further work on this problem unless the water content of the tar gets out of hand again.

NHK:hmw NHK

Attachment

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