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UNIVERSITY OF LOUISVILLE

REMOVAL OF BENZENE-INSOLUBLES FROM COAL TAR
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A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

John W. McKenna
///

September, 1947

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REMOVAL OF BENZENE-INSOLUBLES FROM COAL TAR**John W. McKenna****Approved by the Examining Committee**

Director	G. C. Williams
	R. C. Ernst
	Guy Stevenson
September, 1947	

TABLE OF CONTENTS

	Page
List of Tables	iv
List of Figures	v
Abstract	vii
Introduction	1
Historical	4
Theoretical	8
Experimental Procedure and Results	15
Summary and Conclusions	37
Literature Cited	40
Acknowledgment	43
Vita	45

LIST OF TABLES

Table		Page
I	Analysis of Working Sample of Tar	20
II	Comparison of Percent Insolubles With Surface Tension of Additive Solvent	23
III	Analysis of Filtered and Unfiltered Tar	33
IV	Effect of Surface Active Agents on Benzene- Insoluble Content	35
V	Effect of Adsorptive Material on Benzene- Insoluble Content	36

LIST OF FIGURES

Figure		Page
1	Filtration Unit Using 400 x 400 Monel Metal Filter Cloth	17
2	X-ray Diffraction Pattern of Amorphous Carbon (Lampblack)	25
3	X-ray Diffraction Pattern of Nitrobenzene Insolubles with Filter Aid	26
4	X-ray Diffraction Pattern of 1,1-diphenyl-ethane Insolubles	27
5	X-ray Diffraction Pattern of Benzene Insolubles	28
6	X-ray Diffraction Pattern of Benzene Insolubles on the Filtered Tar	29
7	X-ray Diffraction Pattern of Toluene Insolubles	30
8	X-ray Diffraction Pattern of Acetone Insolubles	31

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ABSTRACT

This thesis is a report of the attempt to remove the benzene-insoluble material from coal tar. After preliminary filtration investigations, it was discovered that the benzene-insoluble material in coal tar consisted of two parts, namely, Carbon I, or material insoluble in the tar itself, and Carbon II, or material that is soluble in the tar but insoluble in benzene. It was demonstrated that the Carbon I could be removed from the tar with the proper use of filter aids, whereas the Carbon II could only be removed by first diluting the tar with benzene to precipitate the insolubles and then filtering to remove the insolubles.

INTRODUCTION

Coal tar is formed by the destructive distillation or pyrolysis of bituminous coal in the presence of a limited amount of oxygen.

Various standards have been set up, and tests originated for the use of coal tar. One such test is the determination of the benzene-insoluble content of the tar. This test is made by diluting a portion of the tar with benzene and filtering. The solids filtered out were termed benzene insolubles. It was thought that these benzene insolubles were a measure of the foreign particles present in the coal tar. Therefore these insolubles were called free carbon.

As the years progressed, newer methods of producing coal tar were introduced and some of these methods produced tars of rather high free carbon or benzene-insoluble content. So this test became a means of determining the type of tar in addition to a standardization procedure.

In the field of wood preserving it was felt that the nature of the free carbon particles hindered the penetration of coal tar into the wood, since the wood acted as a filter. The free carbon piled up at the surface of the wood and retarded further impregnation.

Accordingly, the American Creosoting Company wished to reduce this free carbon, or benzene-insoluble content to 0.5 percent or less. To be economically feasible the mechanism was to be of such a nature that approximately 900 gallons per hour were to be clarified.

Normally the easiest method of removal would be filtration in some form. Hence, the problem resolved into finding a suitable medium which would retain these particles, and still be porous enough to allow the viscous tar to flow through, and then, by adjusting operating conditions, to obtain the desired rate.

HISTORICAL

The discovery of coal tar was first disclosed (1) by a patent taken out in England on August 19, 1681, by Joachim Becher and Henry Serle. In the patent is found the first description of coal tar and coal tar pitch, as well as the methods of production. Coal tar was not used until 1722 when P. J. Marperger originated tarred roofs in Germany. His method was to first caulk the boards with oakum and then sprinkle alternately with tar and a mixture of sand and iron slag. Then in 1746 an English patent was granted to Henry Haskins for a process of extracting spirits from tar and obtaining a very good pitch. This process consists of our present process of fractional distillation in a closed retort connected with a worm condenser.

After about 1780 tar was used extensively to impregnate paper and wood for use as roofing. By 1822 the tarred shingles were made fire-resistant by treating the tar with unslaked lime and surfacing with sand. By that time the tarred or prepared roofing was replacing the straw and wooden shingle. At about the same time William Murdoch of England began to manufacture coal tar on a large scale.

In 1815, F. C. Accum, of England, made use of Haskins' early patent by subjecting coal tar to fractional distillation on a commercial scale. The naphtha that he produced was used in the manufacture of India rubber goods, for burning in open lamps and for certain kinds of varnish. The pitch that remained was consumed as fuel.

The use of tar for weatherproofing continued, and by 1832 tar was used for macadamizing roads in England and also for the manufacture of tar-concrete paving blocks.

The use of coal tar and coal tar distillates for preserving materials was extended to include impregnation of wood that was to be exposed to the weather and other decaying conditions. This was first accomplished commercially in 1838.

These early uses of coal tar have continued and are still the main uses at the present time. The use of tar for roads, roofing, and for weatherproofing consume 80% of the tar produced.

Coal tar is produced commercially in the United States (2) by the following methods: by-product coke oven, vertical retort, horizontal retort, Curran-Knowles process, and low temperature carbonization. However, about 97% of the tar produced is manufactured by the by-product coke ovens.

In the by-product coke ovens substantially all the tar, before it leaves the ovens, is heated sufficiently to decompose the paraffins, naphthenes, and high-boiling tar acids originally present in the primary tar liberated from the coal. This forms in the tar substantial amounts of naphthalene, anthracene, other hydrocarbons, and free carbon. Also if the tar leaving the coal charge is heated too high or too long in the free space above the charge, decomposition of some of the tar constituents occurs with the formation of free carbon in the tar.

The American Greoseting Company (3) realizing that the high amount of free carbon present in coal tar might affect the degree of tar impregnation in wood, constructed a pilot plant in Russell, Kentucky, to attempt to remove free carbon or synonymously, benzene-insolubles, from the tar. The filtering unit employed the use of an electrophoretically charged metal filter cloth (4). This filter cloth was 750 x 50 mesh Monel metal electrically charged with the same polarity as the free carbon in the tar. This was expected to keep the charged fine particles from clogging the screen. The process was to be continuous until the filter cake filled the collector box in the bottom of the unit. This was sufficient to filter one tank car of tar.

After preliminary failures, the cloth was chromium plated to reduce the screen openings. This, however, failed to work as the metallic gaskets did not hold, and some holes were noted in the filter cloth. After repeated failures the project was abandoned.

Many patents have been granted for methods of removing solids from tar and tarry substances. These include flash evaporation (5), additions of pre-coat of the same nature as the filtered solids (6,7), filtration through an electrically charged filter (8), and by using a form of steam distillation (9). All these patents claim the removal of the solid particles or carbon particles from coal tar, but do not mention the removal of benzene-insolubles.

THEORETICAL

Despite the increased interest in the properties of high-temperature refined tar and the improvements which have taken place in methods of preparation during the last few years, very little information exists on the physical and chemical constitution of coal tar. There is much uncertainty as to the physical and chemical nature of free carbon as it exists in coal tar. Such information is, however, essential to an understanding of the changes occurring in tar during its manufacture and use if further improvements are to be made. There has been little study of the determination of insoluble matter in coal tar, although many methods have been proposed for estimation of free carbon in the tar. The fact that only part of this free carbon can be removed by filtration indicates that it may be in a finely divided state, or may be a heterogeneous thing itself.

Houdurek (10) was one of the first investigators to filter tar without the aid of a solvent and to differentiate between the suspended material in tars and the solvent-insoluble material in filtered tars. He found the amount of material dispersed in tar that is insoluble in the tar itself, which he called Carbon I, by using anthracene oil as a diluent. The amount of tar-insoluble material determined in this manner compares favorably with the amount which may be removed from the tar directly by filtration.

Houdurek then distinguished between this Carbon I and the bituminous material, which he named Carbon II, which

is soluble in the tar but precipitated by certain solvents. The Carbon II was precipitated by benzene, toluene, xylene, carbon tetrachloride, and acetone, but not by aniline, quinoline, nitrobenzene, cresol, and anthracene oil.

According to Abderhalden (11) a portion of the free carbon, or Carbon II using Houdurek's nomenclature, existed as an emulsion, with the emulsifying agent being the pitch oils present in the tar. Upon further investigation Monroe and Braderson (12) found that upon digesting tar with solvent at room temperature, the solids content increased gradually with time. Since there was no rise in boiling point, they concluded that there was no chemical reaction, and therefore the solids precipitated because of the dilution.

Other investigators have studied the effects of various solvents on the insoluble content of tar, and have found that Carbon I may also be separated by tetralin (13, 14) and an alkali humate (15).

Carbon I has been described by Mallison (16) as a kind of filler which gives a certain stability to the tar system. The particle size varies from microscopic to ultra-microscopic, and these finely dispersed particles determine the adhesive and binding properties of the tar.

Nellensteyn (17) also attached great significance on the number of visible particles in a given volume of tar. He contends that a nitrobenzene dispersion micron count, i.e., number of visible particles per cubic millimeter of tar, aids

in the classification of tars and is a measure of their binding power. There has been much discussion about his tests with the result that it is now included in the specifications of some countries.

Fein, Eisner, Cooper, and Fisher (18) state that Carbon I contains much ash and carbon with very little hydrogen. It probably consists of the fusain and apaque attritus of the original coal. These are hard to liquify by hydrogenation.

The amount of solvent-insoluble material in tar, or Carbon II, is a function of the solvent used for precipitation, and various investigators state that the Carbon II content depends upon the surface tension of the solvent used. Mallison (19) and Volkmann, Rhodes, and Work (20) along with several other authors (21, 22, 23, 24) state that solvents with low surface tension precipitate the greatest amount of solids, while high surface tension solvents merely act as dispersing agents and do not precipitate the material. Duriez (25) further states that according to the surface tension theory there will always be some Carbon II precipitated no matter which solvent is used. However, the amount will be low for some solvents. These solvents all have very high surface tension.

Duriez was one of the first investigators to report that tar is a colloidal system of resinous micelles in an oil dispersion. He maintained that the stability of the dispersion depended upon the surface tension of the whole. A lowering

of this surface tension produced flocculation of part of these micelles. Nellensteyn (21) goes further in stating that there exists a certain critical surface tension below which Carbon II is flocculated and above which only Carbon I is present.

Duriez also noted the two distinct types of insoluble matter. He stated that the insoluble matter is always composed of two parts: insoluble carbon, the proportion of which is constant for all solvents of the same tar, even if it is filtered hot and under pressure without the use of solvents; and another part, the nature and quantity of which depend upon the solvent used.

Carbon II, or benzene-insoluble material, was isolated by Houdurek (10), and he described it as fusible and capable of great binding strength upon solidification. He concluded that this portion of the benzene-insoluble fraction was an indication of binding strength. Later, Kluckmann (26) stated that the benzene-insoluble contained resinous constituents which are solely responsible for the adhesive quality of the tar.

The modern theory of the constitution of coal tar has been presented by Dickenson (27), and he also states that tar is a colloidal system. The indirect evidences to support this theory were given as: 1) the high temperature susceptibility of the viscosity can be explained only by the change with temperature of the degree of dispersion of the units formed by dispersion; 2) the behavior of the tar fractions in

benzene and the change in viscosity with increase in concentration of Carbon II indicated a colloidal nature formed by association. Only recently has any direct evidence of the existence of these units been found. The electron microscope was used by Dickenson to study the structure of coal tar.

His studies showed tar to be in an "associated colloid" state. The particles observed from the electron microscope appear to be the nuclei of micelle units consisting of the more associated high-molecular resins and carbonaceous particles of colloidal dimensions. These nuclei are surrounded by a solvation layer of the lighter resins, the molecular weight and carbon/hydrogen ratio decreasing continuously from the core to the continuous oil phase of the tar. There is no abrupt discontinuity of phase between the oil medium and the nuclei of the micelles. The intermediate resins which form part of the solvation layer are essential for obtaining a colloidal dispersion of the Carbon II fraction.

The existence of this structure explains the dependence of viscosity on temperature as being due to the change in the degree of dispersion of the associated molecules or the decrease in the size of the micelles. This conception of the stabilizing solvation layer of tar resins surrounding the core of the micelle units gives a simple explanation of the flocculation of tars by certain solvents, and the reasons some tars are more stable to flocculating agents than others.

The action of solvents in the tar system is a combin -

action of dispersing and coagulating action on the tar micelle. The action of benzene would appear to be the removal of the greater part of the protecting layer of resins from the micelles, producing a dispersion of these resins and leaving the nucleus of the micelle unprotected. These nuclei then coagulate and may be removed by filtration. The action of solvents like nitrobenzene is merely a dispersing action without removal of the protecting layer. The micelles then do not coagulate and hence can not be removed by filtration.

Dickenson states that there is also present in tar relatively large, unsolvated particles which correspond to Carbon I. This fraction exists for the most part in the form of a visible dispersion above colloid size. These particles can be removed from tar either by filtration or by sedimentation at high temperatures. The particles of Carbon I can hold a small proportion of the Carbon II by adsorption, so that removal of the filterable Carbon I may produce a substantial reduction in viscosity.

EXPERIMENTAL PROCEDURE AND RESULTS

a. Apparatus

Even though previous investigations illustrated the difficulty of reducing the benzene-insoluble material, it was nevertheless desirable to attempt a mechanical filtration of the raw tar before attempting treatment of the tar in some way prior to filtration. This was even more highly desirable since a new 400 x 400 mesh metal (Monel) wire screen was newly available on the commercial market and represented the smallest pore size yet available. Accordingly, a filtration unit was constructed.

This unit consisted of two tanks, a pump, a flanged fitting for holding the filter cloth, the filter cloth, pressure gages, thermometer, and a piping arrangement as shown by the accompanying diagram, figure 1.

The two tanks were mounted on tripods. One tank was used as a heating tank, the other a receiving tank. Heat was supplied by an electric hot plate. Both tanks were covered to minimize loss of volatile material.

The pump was a gear positive displacement type capable of delivering one gallon per minute at 100 pounds per square inch. The pump was equipped with a built-in by-pass valve by which the maximum pressure was set.

The 400 x 400 mesh filter cloth was backed on each side by a 50 x 50 mesh brass screen. On the outside there was a 16 x 16 mesh brass screen on each side for greater strength. These were all soldered together to fit as one unit. The filter

Figure 1 Filtration Unit Using 400 x 400
Monel Metal Filter Cloth

cloth unit was placed between two flanges in the piping system along with asbestos gaskets, and the flanges were bolted together.

The piping was so arranged that tar could be taken by suction from either tank and could pass through the filter in either direction; the filtered material was then pumped into the opposite tank. The piping was lagged with a layer of one inch wool felt and the complete unit was mounted on a wooden base.

To test the effect of filter aids, a Sparkler horizontal plate filter was used. It was model 8-3, with four horizontal plates, totaling a filtering area of one square foot. The filter paper used on the plates was Sparkler #31 standard.

b. Procedure and Results

The benzene-insoluble content was used as the standard of all tars. The procedure followed in this investigation was that described in the American Wood Preservers Association Manual, test 8b, method 2. This procedure consisted in dissolving a weighed sample of tar in warm benzene, filtering it through a Gooch crucible with an asbestos mat, and washing the benzene until the washings were clear. However, there was a tendency for the asbestos filter to absorb the filtrate with the result that greater quantities of benzene were necessary before the washings were clear, causing difficult

reproducibility. Therefore, a porous bottom glass filtering crucible was used in place of the Gooch crucible. Much less benzene was needed to wash the solids, and the filtering crucible gave more reproducible results.

Other analyses were of Carbon I and Carbon II.

Carbon I was determined according to a procedure described by Rhodes (2). This consisted in dissolving a weighed sample of tar in nitrobenzene, mixing with 1% filter aid, and filtering through a filtering crucible. The cake was washed with nitrobenzene until the filtrate was clear, and finally with benzene. The solids were dried, weighed, and the filter aid subtracted. The resultant solids weight represented the material insoluble in the tar, which could be removed by filtration.

Determination of Carbon II was also a procedure described by Rhodes. A weighed portion of the tar was dissolved in benzene or acetone, filtered through a filtering crucible, and washed with the appropriate solvent. This procedure was similar to the American Wood Preservers Association method described above. The Carbon I content was subtracted from this benzene-insoluble or acetone-insoluble content and the result reported as Carbon II. This Carbon II represented that portion of the tar actually precipitated by the benzene or acetone. Carbon II referred to will be on the benzene-insoluble basis unless otherwise noted. A summary of the results on the tar used in this investigation is shown in Table I. This tar is a by-product coke oven tar with a specific gravity of 1.158

Table I

Analysis of Working Sample of Tar

Carbon I	1.85%
Benzene-Insoluble	6.23%
Carbon II	4.38%
Carbon II (acetone)	9.85%

The experimental filtration unit was used to test the effect of simple filtration on the tar. The operation of the unit was as follows: The heating tank was filled with tar, and heated to 300°F. with an electric heater to reduce the fire hazard. The hot tar was then pumped through one side of the unit and back into the heating tank. This operation served to heat the unit. When the unit was hot the tar was directed through the filter. Pressure was regulated by the valve in the by-pass line. Filtration was continued until the pressure increased to 80 pounds per square inch. The proposed operation was then to draw suction from the receiving tank and reverse the flow of the tar through the filter, dislodging the cake, and collecting the sludge in the heating tank. The cycle would then be repeated. However, after a hour under pressure, only a few drops were filtered and the reversing technique could not be accomplished. There was, however, enough product for an analysis. This filter tar has a total benzene-insoluble content of 7.49, which is somewhat higher than the value for the unfiltered tar. This increase in solids content was probably due to loss of tar by volatilization, and to material pickup in the piping, although the pipe was flushed out before being assembled. It appeared from this run that the filter area was too

small and the long piping system did not hold the heat in the tar, even though the pipes were lagged. The loss of heat and also the loss of volatile material in the tar tended to make the tar too viscous to pass through the fine openings in the filter cloth. It was, however, also evident that the tar could not be filtered directly without the addition of aids for filtration, since the particle size was extremely fine, and blinding of the pores was inevitable.

In order to test the effect of a filter aid, and also to increase the filtering area, the Sparkler filter was used. The filter aid was #503 Celite made by Johns-Manville. This filter aid had a high flow-through rate, but only a fair clarifying rate.

A two gallon sample of the tar was heated in an open bucket and then pumped through the filter unit at a pressure of 20 pounds per square inch. The pressure was regulated by a valve in the pumps by-pass line. The portion of tar remaining in the unit was scavenged through a scavenging plate by air pressure. The rate of flow during the filtration was approximately one gallon per minute. An analysis of the product gave the total benzene-insoluble content as 7.0%. This increase in solids was probably due to presence of filter aid in the filtered tar. It was evident that this filter aid was not fine enough to remove any solids from the tar although it did give the flow rate desired.

It was desirable to study the effect of other solvent

on the nature of coal tar. Accordingly, an extraction battery was set up to test the solvents. The unit contained six flasks each of which contained Soxhlet extraction cup containing an extraction thimble. A weighed sample of tar was placed in the coned filter paper and placed in the thimble. The solvents were placed in the bottom of the flasks. Heat was supplied by electric lights placed under each flask. After three days of continuous extraction the drippings from the units containing acetone, toluene, and benzene still showed an amber color, while those of methyl alcohol, hexyl alcohol, and kerosene showed no effect of extraction. In all cases it was noted that the tar has a tendency to "creep" through the filter paper and thimble into the solvent at the bottom of the flask. Other attempts were made using a fine pore Alundum extraction shell in place of the extraction cup and thimble, and using an electric hot plate instead of electric lights. Both of these met with the same difficulties.

It was therefore decided that a method be used similar to the American Wood Preservers Association test for benzene-insolubles. The solvent to be tested was added to a weighed portion of the tar, the mixture warmed, filtered through a porous filtering crucible and washed with the solvent. With the nitrobenzene, diphenylethane, and xylene dilutions an additional wash with benzene was made to facilitate drying. The solids were dried, weighed, and reported as percent insolubles. There were some solvents tried - methyl alcohol,

hexyl alcohol, kerosene, naphtha, and petroleum mineral spirits -in which the tar was almost completely insoluble. The tar seemed to be more insoluble in aromatic solvents than in aliphatic solvents.

The various solvent insoluble contents together with the surface tension of the solvent are presented in Table II. The values of surface tension were obtained from the International Critical Tables (27).

Table II

Comparison of Percent Insolubles With
Surface Tension of Additive Solvent

Solvent	% Solvent Insolubles	Surface Tension @ 20°C.
Nitrobenzene	1.9%	43.9 dynes/cm.
1,1-diphenylethane	5.2%	37.7 "
Benzene	6.2%	28.9 "
Toluene	6.4%	28.4 "
Xylene	7.7%	28.9 "
Acetone	10.5%	23.7 "
Carbon Tetrachloride	10.6%	26.8 "

As was expected from the surface tension theory, it was found that various solvents had widely different insolubilizing effect on the coal tar, and as is indicated in Table II, there was a rough correlation between the surface tension of the solvent and the insoluble content. In general, the higher the surface tension the lower the insoluble content. Nitrobenzene with the highest surface tension gave the lowest insoluble content; and acetone with the lowest surface tension, gave one of the highest insoluble contents. There was some difficulty in obtaining reproducible results with acetone and carbon tetrachloride owing to the extreme volatility of these

solvents.

Since the values for nitrobenzene and diphenylethane-insolubles were lower than that for benzene, a qualitative test for benzene-insolubles was made, using the filtrate from the filtration of the two insolubles. Upon the addition of benzene to the filtrate, particles were formed which were filtered using a porous bottom filtering crucible. The amount of solid material present was comparable to the difference in solids content between benzene and nitrobenzene or diphenylethane. This constituted a fair check of the validity of the test.

To further study these solvent insolubles, x-ray diffraction patterns were obtained from the residual solids from the solvents, benzene, toluene, acetone, 1,1-diphenylethane, and nitrobenzene, as well as amorphous carbon (lamp black). A sample of the solids was placed on the x-ray machine and held in place with transparent tape. The film to be exposed was placed 20 centimeters from the sample, and a shield was placed in the direct ray to eliminate the possibility of the ray burning the film. This shield may be seen in the patterns. The x-ray diffraction patterns are presented in figures 2-8.

There was no detectable difference between any of the diffraction patterns. There were no distinct rings as produced by crystalline substances, and only a fuzzy band appeared near the center of focus. This result was probably due to the amorphous nature of the solids. However, there

Figure 2

X-ray Diffraction Pattern of Amorphous
Carbon (Lampblack)

Figure 3

X-ray Diffraction Pattern of Nitrobenzene
Insolubles with Filter Aid

Figure 4

X-ray Diffraction Pattern of 1,1-diphenylethane
Insolubles

Figure 5
X-ray Diffraction Pattern of Benzene
Insolubles

Figure 6

X-ray Diffraction Pattern of Benzene
Insolubles on the Filtered Tar

Figure 7

X-ray Diffraction Pattern of Toluene
Insolubles

Figure 8

X-ray Diffraction Pattern of Acetone
Insolubles

was strong indications that the solids were not widely different in nature. This result also gave evidence to the theory that the solvent insoluble solids were of the same resinous nature and differed merely in quantity with the different solvents.

It became more evident that tar is a colloidal system, and that only Carbon I, or tar-insoluble material, could be removed by filtration in some form. Since it was shown that the Carbon I could not be removed by ordinary filtration with a filter cloth alone, it was decided that the finest size commercially available filter aid be tried. This was Johns-Manville Filter-Cel. It was felt that these tests should be conducted on a laboratory scale. Accordingly, a laboratory type suction funnel, or Buchner funnel, was used with Sparkler #31 standard filter paper.

The tar was heated to 250-280° F. and 1% by weight of Filter-Cel added. The tar was filtered while hot. The filtrate was collected in a test tube within the suction flask. The first portion of the filtrate was discarded, and only the last portion of the filtered tar was used for analysis. Filtration was rapid at first, but quickly slowed down as the tar in the funnel cooled. Only about 10 milliliters were filtered before the filter plugged up and filtration ceased. Carbon I and Carbon II determinations were made on the filtered tar. A summary of the results are shown in Table III.

Table III

Analysis of Filtered and Unfiltered Tar

	Unfiltered Tar	Filtered Tar
Carbon I	1.85%	0.42%
Benzene-Insoluble	6.23%	5.3 %
Carbon II	4.38%	4.9 %

The values presented for the filtered tar are a little high because some of the more volatile constituents in the tar evaporated when the hot tar was subjected to the vacuum, and there is also some indication of filter aid contamination of the filtered tar, however duplicate filtrations checked these values very closely.

It can be seen that filtration with Filter-Cel as the filter aid materially reduces the Carbon I content of the tar while Carbon II remains practically the same. It can be stated, therefore, that the Carbon I, or tar-insoluble particles, can be removed by the addition of a fine size filter aid followed by simple filtration with a standard filter paper.

It was thought that since benzene was used in the determination of benzene insolubles, the addition of a smaller amount of benzene might agglomerate the Carbon II particles sufficiently to effect their removal by filtration. It was hoped that the amount of added benzene might be below that necessary to affect the properties of the resultant tar. Arbitrarily 8% of benzene was established as an upper limit for this action and accordingly, benzene in the amounts of 1%, 5% and 8% was added to the tar along with Filter-Cel filter aid.

The resulting solution was then filtered as before. The filtrates were analyzed for Carbon I and Carbon II. The Carbon I content was only reduced to 0.2%, whereas the Carbon II content was not reduced, with the addition of 8% benzene. It was evident that more benzene than can be disregarded in the final product must be added to remove all of the Carbon II content.

It has been stated that the stability of the micelle dispersion of the coal tar is thought to be dependent upon the surface tension of the tar. To test this theory, various surface active agents were employed in an effort to reduce the surface tension below the critical surface tension and agglomerate the micelle units. If the surface tension were lowered enough, the benzene-insolubles would flocculate and could then be removed by filtration. The surface active agents were used in the amount of 5% by volume, since it was felt that this was the greatest amount that could be added to the tar without affecting the properties of the resultant tar. Each agent represented a class of surface active agents known to reduce the surface tension of oils. The following were used: diglycol laurate (an ester of ethylene glycol), Span 80 (a partial ester of sorbitan), triethanolamine (an amine), calcium oleate (an oil-soluble soap), and sodium oleyl sulfate (a sulfonated fatty acid). The agent was added to a portion of the tar, the mixture heated to 230-250°F., 1% of filter aid (Filter-Cel) added, and the mixture filtered through a suction funnel with #31 Sparkler filter paper as before. Only the last portion of the

filtered tar was used for analysis for benzene-insoluble material. The results are presented in Table IV.

Table IV
Effect of Surface Active Agents on
Benzene-Insoluble Content

Surface active agent	% Benzene-insoluble
Diglycol laurate	4.4%
Span 80 (Atlas)	5.0%
Triethanolamine	5.3%
Sodium oleyl sulfate	6.3%
Calcium oleate	6.5%

As is indicated in this table, the addition of a surface active agent does not reduce the benzene-insoluble content much below that of filtered tar, namely 5.3%. This is probably due to the inability to lower the surface tension low enough with the small addition of surface active agent, or that the theory cannot be extended to this tar.

Since it had been reported that Carbon I did adsorb some Carbon II, and remove some of it by filtration, it was felt that some other adsorptive material might selectively adsorb these micelle units from their protective layer thus permitting their removal by filtration. Accordingly, activated charcoal and activated alumina were used along with 1% of filter aid. The procedure for filtration was the same as that used in testing with the surface active agents. The results are shown in Table V.

Table V

Effect of Adsorptive Material on
Benzene-Insoluble Content

Material added	% used by weight	% Benzene Insoluble
Activated charcoal	2 %	5.2%
Activated alumina	5 %	4.9%

These activated materials also failed to lower the benzene-insoluble content of the filtered tar. This was probably due to the fact that the activated materials were not of the same nature as the Carbon I.

SUMMARY AND CONCLUSIONS

It has been reported and reasonably confirmed that coal tar is a dispersion of associated micelle units in an oily medium. These micelle units have a protective solvation layer of intermediate resins surrounding them. There are also present in the tar system small unsolvated particles which are insoluble in the tar itself. This is called Carbon I. The colloidal particles or micelles which are dispersed in the tar can be coagulated by the addition of a large amount of certain solvents. The solvent disperses the protecting intermediate resins and the unprotected micelles coagulate to form large particles which can be filtered out. The amount and nature of the coagulated particles is dependent upon the solvent which is used. These particles are Carbon II. The problem was to remove the material which was insoluble in benzene.

Preliminary filtrations with a 400 x 400 mesh Monel metal filter cloth and with a Sparkler horizontal plate filter with #503 Celite filter aid showed that the benzene-insoluble content was not reduced. However, filtration with a finer size filter aid, Filter-Cel, with a laboratory suction funnel reduced the Carbon I content from 1.9% to 0.42%, while the Carbon II content remained practically the same. It was obvious that some other treatment was necessary in order to remove the Carbon II, or benzene-insoluble, tar-soluble material.

Other treatments tried were the addition of small amounts of benzene, surface active agents and the addition of adsorptive materials. These methods did not reduce the Carbon

II content below that of the filtered tar.

It is recommended, if Carbon I only is to be removed, that the tar be heated to 250 -300 F., Filter-Cel added as a filter aid, and the resulting mixture filtered through a suitable filter. This recommendation is based on filtration with a laboratory suction funnel using the above conditions.

It is further recommended that if Carbon II must be removed, the tar be diluted with benzene, mixed thoroughly, the mixture filtered through a suitable filter, and the benzene reclaimed in some manner, such as distillation. The dilution ratio of benzene to coal tar would be high, in the neighborhood of fifteen to one. Inasmuch as this is a large amount of benzene to be added, it is not known what effect the addition and subsequent removal would have on the resultant tar. The proper limitation for removal of benzene would create a second problem since there are tar constituents that boil about the same range.

The effect of the removal of Carbon II on the physical characteristics of the tar has not been determined.

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