

DEPARTMENT OF THE INTERIOR

ALBERT B. FALL, SECRETARY

BUREAU OF MINES

H. FOSTER BAIN, DIRECTOR

# PREPARATION AND USES OF TAR AND ITS SIMPLE CRUDE DERIVATIVES

BY

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ILLINOIS COAL-MINING INVESTIGATIONS  
COOPERATIVE AGREEMENT

[This report was prepared under a cooperative agreement with the  
Illinois State Geological Survey and the department of  
mining engineering of the University of Illinois]



WASHINGTON  
GOVERNMENT PRINTING OFFICE  
1922

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*First edition, February, 1922.*

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# THE PREPARATION AND USES OF TAR AND ITS SIMPLE CRUDE DERIVATIVES.

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By W. W. ODELL.

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## INTRODUCTION.

The importance of tar as a commercial product has been emphasized during the past five or six years more than ever before. In that time, the market for tar and its products fluctuated in an unprecedented way, because of the war and other conditions, with the result that the production of tar and tar products increased greatly. A large proportion of the increase is due to the installation of by-product coke ovens, which are fast replacing the beehive ovens, from which tar and other by-products are not recovered. The increasing demand for steel and the shortage of anthracite coal during the war were a great impetus to the coking industry. In 1920 tar was being produced in greater quantities than ever before, but the entire output was not on the market for sale, as increasingly large quantities were being used for fuel. However, in some localities where the output of tar was small or was of inferior quality—particularly water-gas tar—there seemed to be no great demand for the product.

This paper discusses the uses to which some of the various tars are put and shows briefly the usual methods of working up tar into some of its simple or easily prepared derivatives, for which a market can generally be found. Although coal tars are given chief consideration, the properties and characteristics of water-gas tar are mentioned, for the reason that this tar is often produced in plants where coal tar is made, the mixed tar being collected and marketed, and for the further reason that the presence of water-gas tar in some coal-tar products is specifically interdicted by commercial specifications. This publication is not a handbook on tar distillation, for that subject can hardly be covered adequately in such limited space, but is published by the Bureau of Mines as a general treatise on the utilization of tar.

## SOURCES, VARIETIES, AND PRODUCTION OF TAR.

### DEFINITION.

Different people have different ideas as to what is meant by tar; some regard it as a black, hard "chewable" substance which is shipped in open barrels and used for roofing buildings (in reality

this is pitch or asphalt). Others think of it as a mysterious substance from which headache powders, colors, dyes, and other chemicals are obtained. Part of the popular misconception regarding the chief uses of coal tar may be due to such definitions of tar as are given in some dictionaries. Although only a small proportion of the tar manufactured is actually used for making drugs, chemicals, flavoring extracts, and headache powders, it is not uncommon for dictionary definitions to state that tar is a black viscous liquid from which these and similar products are obtained. According to Webster's dictionary:

Tar is a thick, brown to black viscous liquid obtained by the destructive distillation of wood, coal, peat, and other organic materials, and having a varied composition according to the temperature and material employed in obtaining it.

From this definition one can readily see that there is a possibility of producing an almost endless variety of tars by distilling substances of a nature similar to wood, coal, and lignite at various temperatures and under different conditions. It does not follow, however, that in order to understand tars one must have a complete knowledge of the chemical differences and exact chemical nature of each one. Some tars are quite similar in many respects, in spite of the fact that they are made under different conditions and contain varying amounts of the constituents that go to make up tar.

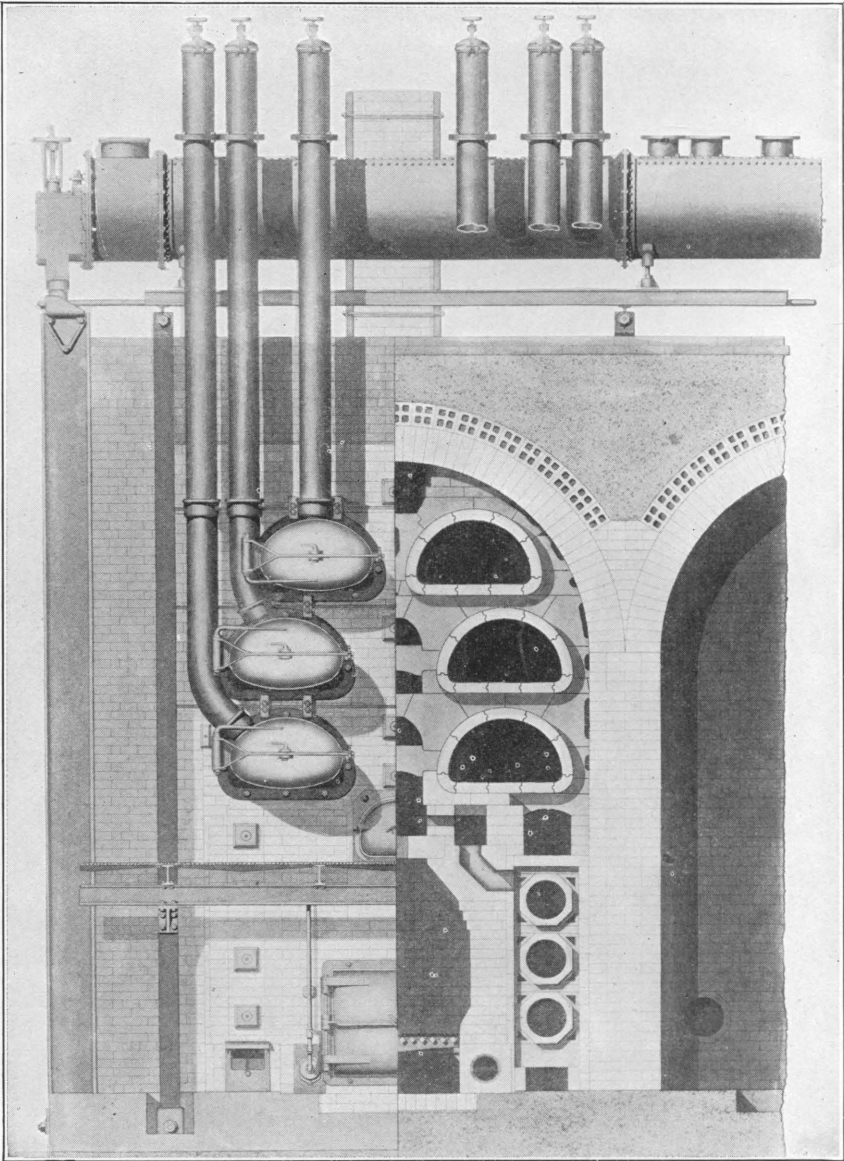
#### CHIEF SOURCES OF TAR.

Although it is possible to produce an endless variety of tars, the varieties commonly found on the market in appreciable quantities are few in number and may be listed under the general heading of tars produced as a by-product in the manufacture of combustible gas or coke as follows: Horizontal-retort tar, inclined and vertical retort tar, by-product coke-oven tar, water-gas tar, producer-gas tar, and oil-gas tar.

In fact, a more general classification can be made, and the chief varieties of tar on the market may be classed as: Coal tar (including retort tar and oven tar), water-gas tar, and mixtures of coal tar and water-gas tar.

#### COAL TAR.

According to definition, coal tar is obtained by the destructive distillation of bituminous coal, as in the manufacture of coal gas. New methods of manufacturing coal gas have been introduced in recent years, which in turn have resulted in corresponding changes in the properties of coal tar. In times gone by coal gas was manufactured by heating coal to 1,200 or 1,500° F. in horizontal clay retorts.



MODERN HORIZONTAL BENCH OF SIX RETORTS. (COURTESY OF THE IMPROVED EQUIPMENT CO.)



Later, silica retorts replaced those of clay and made possible the use of higher temperatures for carbonizing the coal in order to shorten the time of carbonization and increase the gas-making capacity of the plant. In other words, by using a higher temperature the coal could be coked and the gas obtained more quickly. Plate I shows a modern type of a horizontal-retort bench of six retorts and portrays the construction of retorts, flues, furnace, and gas offtakes or stand-pipes. In the past the by-products of coal were not given the serious consideration that they receive to-day, and less attention was paid to the properties of tar and to the conditions governing or affecting these properties. The advent of the vertical retort brought a further change in the properties of coal tar, as the length of time that the heavy vapors distilled from the coal are in contact with the hot chamber walls is not the same in vertical retorts as in horizontal retorts. In the vertical retorts the coal is charged periodically at the top and the coke is removed periodically at the bottom. Plate II shows a vertical section and elevation of a modern vertical retort system.

#### BY-PRODUCT COKE-OVEN TAR.

By-product coke-oven tar is a particular kind of coal tar. In by-product ovens coal is carbonized in greater mass and the carbonization period is longer. Although the common gas-house practice is to carbonize coal in retorts for 4 to 8 hours, the average time of carbonization in the by-product coke industry is 18 hours. In by-product ovens the coal is not heated so rapidly, but it is finally exposed to a higher temperature, resulting in the production of a greater volume of gas and a different quality of coke and tar. Plate III shows a battery of Koppers coke ovens with coke being pushed from one oven into the quenching car.

#### WATER-GAS TAR.

In the manufacture of carbureted water gas about half a gallon of tar is produced as a by-product for each thousand feet of gas made. Coal is not the source of this tar, however, as it is not the common practice to use coal as fuel in the manufacture of water gas, for this gas is produced by forcing steam through a body of incandescent coke rather than coal. The steam is decomposed and reacts with the carbon, with the resulting production of carbon monoxide and hydrogen. The gas usually produced is not rich enough in illuminants to meet most standards for city gas and has to be enriched by carbureting, that is, by spraying oil into the gas in chambers containing red-hot checker bricks. The high temperature volatilizes the oil, and fixes it as a gas. Some heavy vapors formed in oil carbureting are not permanent gases but condense out of the

gas on cooling. The liquid so condensed is known as water-gas tar. Plate IV shows a complete carbureted water-gas set.

The properties and nature of water-gas tar naturally vary according to the temperature of the checker-brick chambers in which the oil is cracked or gasified, the rate at which oil is admitted to these chambers, the kind of oil used, the size of the checker-brick chambers, and other variables.

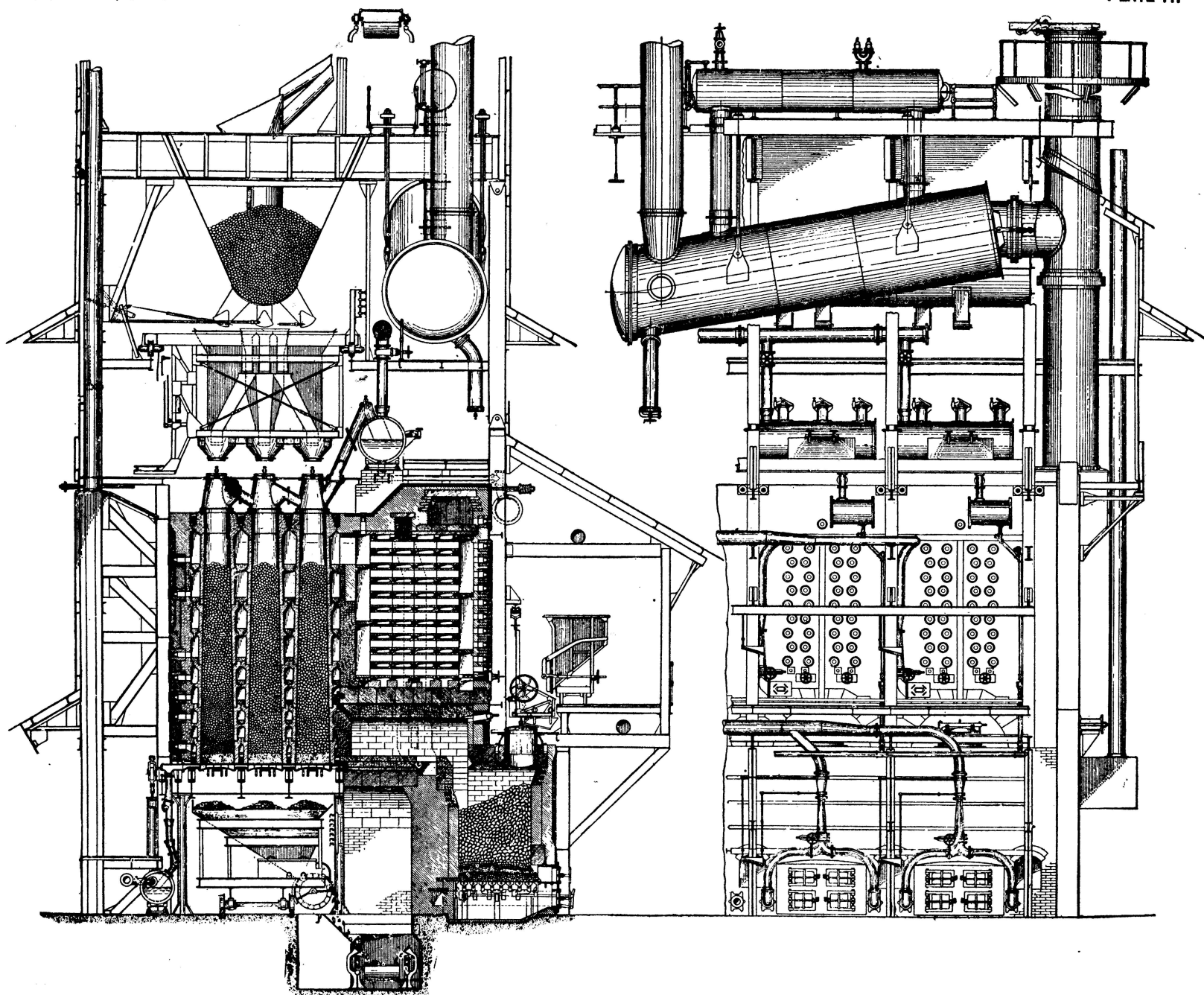
## PROPERTIES OF TARS.

### COAL TAR.

#### RETORT-GAS TAR.

Retort-gas tar, which is obtained as a condensation product in hydraulic mains, scrubbers, and condensers in the manufacture of illuminating gas by the carbonization of bituminous coal in retorts, is a black viscous liquid that contains less of the lighter hydrocarbons and more anthracene, naphthalene, heavy hydrocarbons, and free carbon than the tars from some other sources. The specific gravity (weight per unit of volume compared with weight of an equal volume of water) of water-free retort-gas tar ranges from 1.10 to 1.25, according to operating conditions in the plant and the kind of coal used. Usually a tar of the higher specific gravity is more viscous and less free-flowing than tar of the lower specific gravities. The so-called "free-carbon" content varies considerably. Tar from horizontal retorts usually contains 18 to 30 per cent of free carbon, whereas vertical-retort tar usually contains less than 5 per cent, and much of it as low as 0.4 of 1 per cent. Tar from inclined retorts does not differ widely in this respect from the product of horizontal retorts, the free carbon content being 12 to 20 per cent. Although it may be said, in general, that these tars have much the same constituents, but in varying proportions, it is to be noted that the horizontal-retort tar with a high specific gravity and high free-carbon content yields an appreciably greater percentage of pitch or hydrocarbons having a high boiling point. Tar obtained by carbonizing coal at low temperatures differs considerably from ordinary retort tar in both chemical and physical properties, and is in some respects much like a mineral oil, although its acid content is very high. So far as the author knows, this kind of tar is not being produced commercially in large quantities, and is mentioned here merely to point out the effect of the temperature of carbonizing on the resulting tar.

Differences between the various tars are in great measure due to the rate, duration, and completeness of heating of the coal, the amount of exposure of the tarry vapors to hot brick or coke surfaces, the temperature of these walls, and the exposure of the vapor to the final temperatures reached in the coking chamber. All of these par-



THE "U. G. I." VERTICAL RETORT SYSTEM.

Courtesy of the United Gas Improvement Co.





ticulars are considered in the design of chambers or retorts for coking coal. Euchene's experiments in carbonizing coal in horizontal retorts have shown that a large proportion of the tar produced comes over in the early stages of carbonization. His results, given in the following table,<sup>1</sup> were obtained when the final average temperature in the carbonized fuel was 950° C. (1,742° F.). Considering the rate of decomposition of the coal to be proportional to the totals given in the table, the amounts decomposed from the first to the last hour are approximately represented by the figures 40, 30, 20, and 11. The tar produced is not proportional to these figures, for the reason that during the later stages of carbonizing, the tar formed in the inner zone of coal has to pass through a zone of hot coke, where much of it is decomposed. Thus one can see that the size and shape of the retort and the manner of removing the gas—which affect decomposition—affect the yield and quality of tar.

TABLE 1.—*Tar, water, and gas produced during carbonization.*

Products.	First hour.	Second hour.	Third hour.	Fourth hour.	Total.
Gas.....	17.3	16.6	14.3	9.5	57.7
Water.....	12.3	7.3	2.9	1.0	23.5
Tar.....	10.1	5.3	2.8	.6	18.8
Total.....	39.7	29.2	20.0	11.1	100.0

The vertical retort tar is thinner, has a lower specific gravity, and contains less free carbon and more tar acids than the tar from horizontal retorts.

## BY-PRODUCT OVEN TAR.

By-product oven tar is less viscous; is lighter in weight—that is, has a lower specific gravity; contains more oils, less pitch, and less free carbon than the tar from horizontal retorts; and in some respects is much like the tar from vertical retorts. Table 2 shows the relative properties of the various coal tars:

TABLE 2.—*Properties of coal tars.*

Properties.	Gas-works coal tars.			Coke-oven tars.
	Horizontal retorts.	Inclined retorts.	Vertical retorts.	
Specific gravity at 60° F.....	1.20 to 1.25	1.10 to 1.20	1.10 to 1.15	1.17 to 1.22
Viscosity.....	High.	Medium.	Low.	Low.
Free carbon <sup>a</sup> (insoluble in benzol)..... per cent..	18 to 30	10 to 20	0.4 to 5	2 to 12
Distillate, per cent by volume, on distilling to a medium grade of pitch.....	20 to 30	25 to 35	30 to 40	25 to 35
Per cent of pitch by volume (medium pitch), plus losses.....	70 to 80	65 to 75	60 to 70	65 to 75
Tar acids..... per cent..	1.6 to 3	3 to 5	7 to 8	0.4 to 2.5

<sup>a</sup> The so-called free carbon, which is a constituent in varying quantities of all tars, is not pure carbon, as the term might lead one to think, but consists of complex relatively insoluble carbon compounds containing approximately 94 to 95 per cent of carbon.

<sup>1</sup> Wagner, F. H., Coal and coke. New York. 1916, p. 293.

### WATER-GAS TAR.

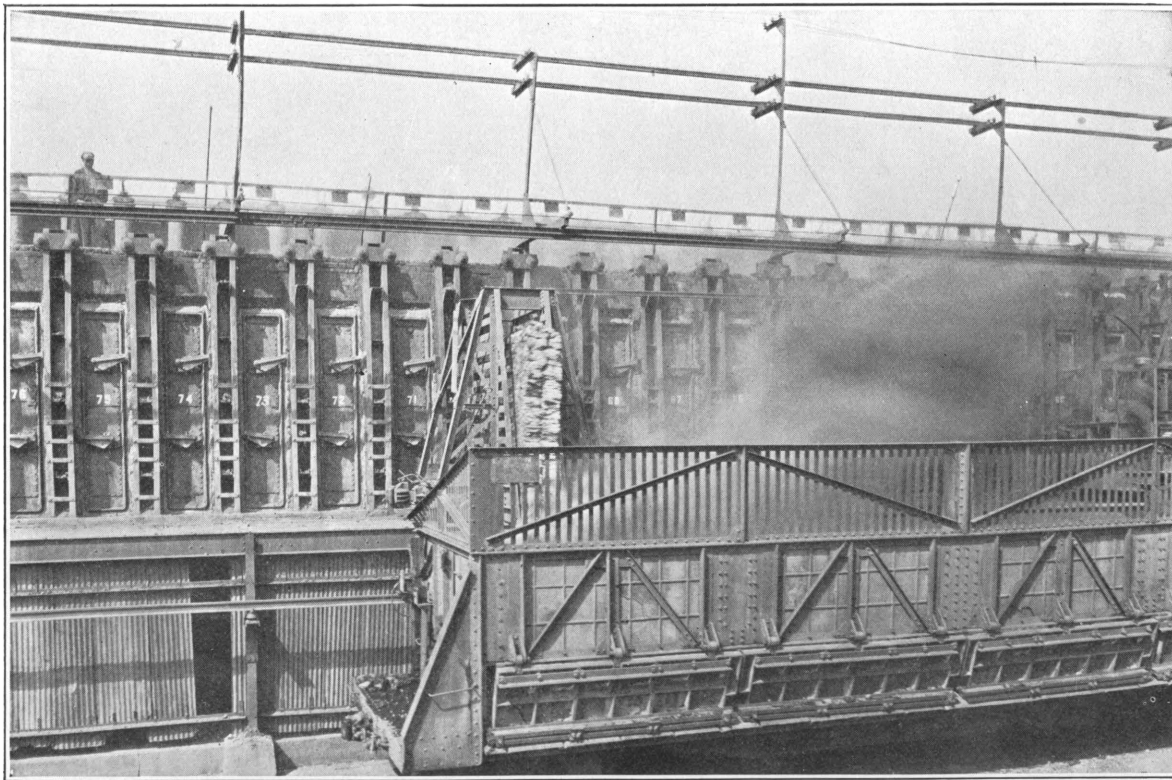
Water-gas tar has an entirely different origin from coal tar and, in addition, differs from coal tar both physically and chemically. In appearance, however, it is much the same, except that it is much more fluid; that is, it has the consistency of water or oil. When a small quantity is rubbed between finger and thumb in a thin layer, it appears to be brown to black. Its specific gravity is very nearly the same as that of water, but when free from water, the specific gravity may be as high as 1.15. Water-gas tar from small gas plants where the gas is produced intermittently varies more, both in composition and in physical properties, than in the larger plants where operation is continuous. Tars with specific gravities little greater than that of water (1.00) are not separated from water as readily as the heavier tars. Frequently, water-gas tars are found that carry considerably more than 50 per cent of water. Such a fluid is, to be specific, an emulsion of tar and water, yet in appearance it is tar. Water-gas tar contains compounds known as paraffins which are not present in coal tar. It is further distinguished from the latter by its not containing any appreciable amount of tar acids. Free carbon is seldom present in amounts greater than 1 to 4 per cent.

### RAW AND REFINED TAR.

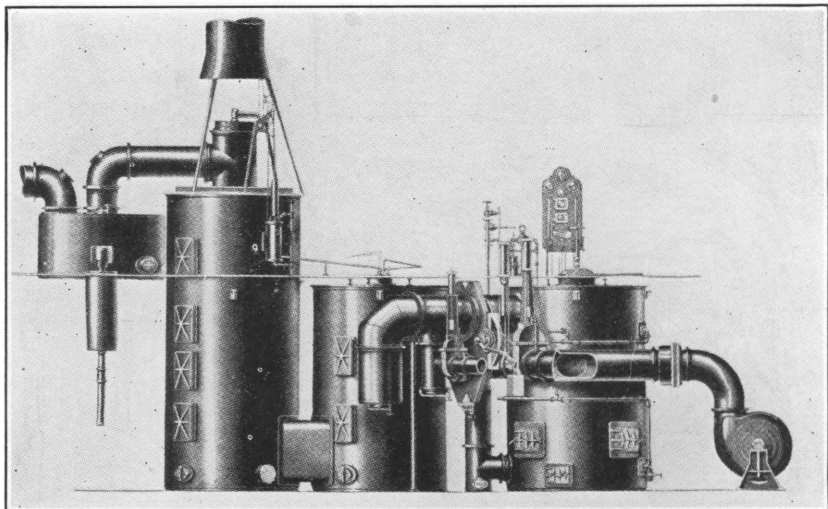
Raw tar is tar as collected at the works; it contains water in various proportions and frequently small amounts of ammoniacal liquor. For most purposes it is desirable that the tar be freed from both of these ingredients, hence it is usually sold to consumers in other than the raw state.

Refined tar has had these ingredients removed by the application of heat. In some plants the tar is heated in vertical tanks by a coil immersed near the bottom; then it is drawn off from the bottom and sold as refined tar. The tar thus treated is not free from water or ammonia but is, perhaps, more suitable for most purposes than the untreated tar. When tar is heated in a closed tank until the water, ammonia, and crude naphtha or "first runnings" are removed, the remaining tar might more properly be termed "refined tar." For certain uses it is desirable to continue the heating a little longer, volatilizing and removing more of the lighter oil constituents of the tar; the resulting heavy tar is also called refined tar. When it is purchased in quantities and when the particular use to which it is going to be put is known, the tar is usually refined to suit a given specification.

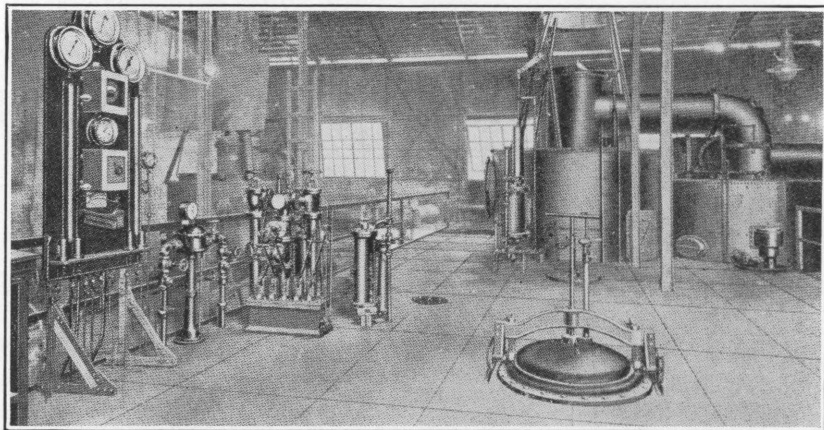
Boiled tar is a name often given to tar that has been refined. The custom prevailed at one time of boiling tar in open vessels



BATTERY OF KOPPERS COKE OVENS, SHOWING DISCHARGE OF HOT COKE INTO CARS. (COURTESY OF THE KOPPERS CO.)



A. COMMON TYPE OF WATER-GAS SET IN USE AT PRESENT.



B. OPERATING FLOOR WITH CONTROL VALVES AND GAGE FOR ABOVE SET.

(usually in small quantities of less than 1,000 gallons) with constant stirring, the heating being stopped when the tar had the consistency desired for any particular purpose. The wastefulness of this practice and the danger from fire, and the small quantity that could be treated at a time have led to the adoption of more suitable means of refining.

Tars that have been refined are heavier and more viscous than raw tar, their viscosity depending on the degree of refining. When refined only to the point where the water is completely expelled, the tars have the relative viscosities given in Table 2. When refining is continued until a large proportion of the oil constituents of the tar have been vaporized and removed, the resultant product is no longer called refined tar but distilled tar, or pitch.

### TAR DISTILLATION.

According to Webster's dictionary, distillation is "the operation of driving off gas or vapor from liquids or solids, as by heat, in a retort or still, and condensing all or some of the products in a cool receiver or condenser." It follows tar distillation means the application of heat to tar contained in a still, whereby vapors are driven off and condensed by coming in contact with cool surfaces or condensers.

#### METHODS.

The simplest way to distill tar would seem to be by means of a direct fire placed beneath a closed tank having a take-off for the vapors and a means of cooling and condensing them. A pipe connected to the top of the still, large enough to carry off the vapors as they are formed, is a simple equipment for removing them. When a part of this pipe is cooled, as by immersion in cold water or by a water spray, the vapors condense to a liquid and the part of the pipe being cooled is called the condenser.

Essentially this method is commonly employed for distilling tar at present. Improvements are frequently made in furnace design for efficient heating of the still, and numerous changes in stills have been suggested from time to time. Various methods have been devised for cooling the distilled vapors, some of which utilize the heat given up on condensing to preheat the tar to be distilled. Other improvements have been made in the process during its evolution, but the fundamental principles are generally utilized in a very simple way.

When heat is applied to tar contained in a still, the first change that takes place is the volatilization of the very light oils and the water contained in the tar. These vapors pass out through the off-

take and are cooled in some suitable and convenient manner. On condensing to a liquid, the light oil and water can easily be separated. As more heat is applied, heavier vapors (the vapors of oils having a higher boiling point) distill off. The application of heat can be continued until finally the volatile oils have all been evaporated and only carbon or coke is left in the still. The oils that distill off from the tar in this manner increase in density (specific gravity) from the beginning to the end of distillation. The character of the residue in the still depends on the extent of distillation; that is, if it is carried to completion, the residue is coke; if the distillation is stopped before all the heavier fractions are vaporized and driven off, the residue is

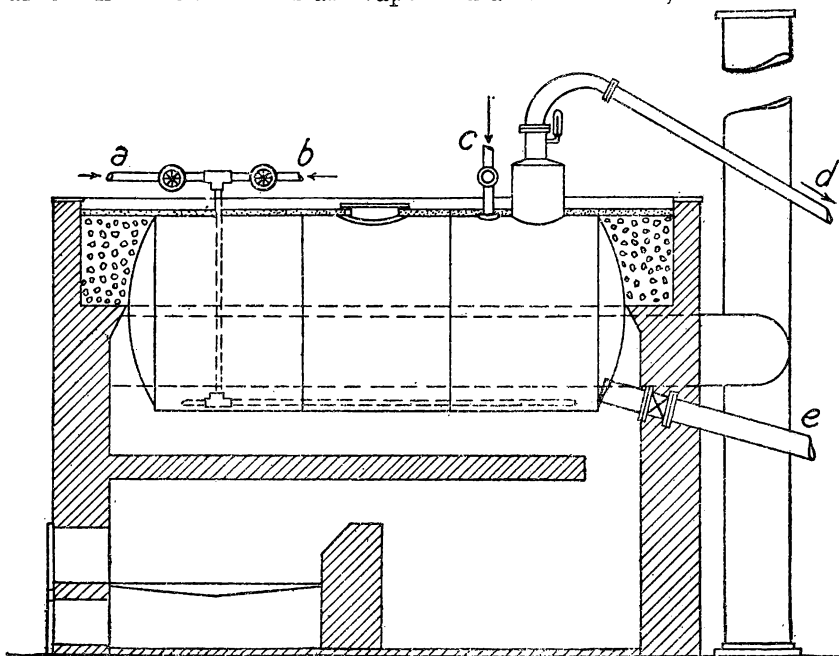


FIGURE 1.—Tar still, common boiler type: *a*, Steam inlet; *b*, air inlet; *c*, tar inlet; *d*, vapor offtake leading to condenser; *e*, pitch offtake leading to cooler.

pitch. The more oil left in the residue, the softer is the pitch, and vice versa.

Distillation may be carried on in various ways. One of the most common types of stills used for this purpose in the United States is a cylindrical horizontal steel shell set in brickwork to protect it from direct contact with the flames, as shown in figure 1. Provisions are made for admitting the tar, removing the vapors, and withdrawing the residue or pitch. A safety valve prevents explosions if the off-take or condenser coils become choked. Air and steam jets are also shown in the figure and are used to finish the distillation after the lighter fractions have distilled off.

In Europe, the vertical still is said to be more generally used. This type, shown in figure 2, consists of a vertical shell of about the same diameter as height, with a concave bottom, set similarly over a brickwork furnace, and having an arch protecting the bottom from the direct action of the fire. The vertical still requires less fuel, and time to distill a definite amount of tar, chiefly because of the increased heating surface exposed to the hot gases from the furnace. In the horizontal type, slightly less than half of the cylindrical surface of the still is heated.

Another still, regarded with favor by some of the companies operating large plants, is a modification of the horizontal boiler type. Large flues pass through the tar lengthwise and the waste-furnace gas—burned gas—passes through these flues before it enters the stack. The superiority of this still is due chiefly, but not entirely, to the increased heating surface—increased for a given size shell—provided by the flues.

Processes, some of which are in use, have been developed for the continuous distillation of tar. The Hird and Wilton systems<sup>2</sup> are said to be very satisfactory. Hird's process utilizes four stills at once, but only a part of the distillation is done in any particular still. The lighter fractions are removed

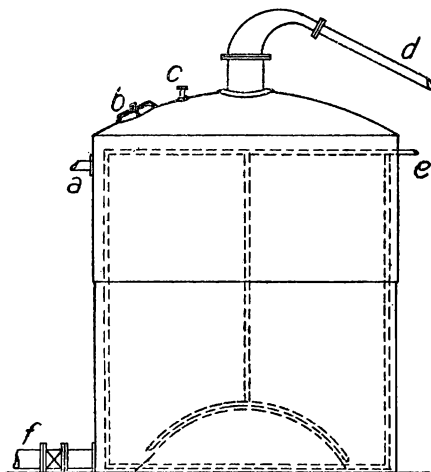


FIGURE 2.—Vertical tar still, European type:  
a, Tar inlet; b, man-hole; c, safety valve;  
d, distillate offtake; e, steam inlet.

from still 1, the next heavier fractions from still 2, and the final fractions and the remaining pitch from still 4. An arrangement of baffles compels the tar in going through a still to pass in a circuitous manner from inlet to outlet. Before entering still 1 the tar is heated by the sensible heat of the pitch; that is, the tar passes through pipes within the pitch coolers before entering that still. In the Kubierschky system,<sup>3</sup> another continuous process that has attracted some attention, the tar is blown into the still in a spray. Superheated steam blown from below comes in direct contact with the tar. The distillation progresses in stages in a series of chambers.

<sup>2</sup> Chambers, E. V., Tar dehydration: Jour. Gas Lighting, vol. 132, 1915, pp. 261-264; Livesey, Frank, Some notes on the partial distillation of tar in a Wilton's continuous still: Pp. 373-375; Wardell, R., Notes on tar dehydration: Pp. 375-377.

<sup>3</sup> Borrmann, C. H., Tar—New methods used in washing and distilling liquids: Ztschr. angew. Chem., Jahrg. 28, 1915, pp. 377-380, 381-388; Jour. Soc. Chem. Ind., vol. 34, 1915, p. 1232.

**SEPARATION OF TAR FROM WATER—DEHYDRATION.**

When tar condenses from illuminating gas there is condensed simultaneously a considerable amount of water. As it is desirable for obvious reasons that the tar be as free from water as possible, a means of making this separation is usually provided at all plants producing tar.

**METHODS.**

The simplest method of separating water is the "settling method," in which quantities of tar are allowed to settle in undisturbed tanks; the tar, being of higher specific gravity, settles to the bottom below the water. At some plants tar is heated to facilitate the separation, heating being particularly advantageous with tars of high viscosity. This method of separation does not afford complete dehydration of the tar; in fact, coal tar so treated contains 2 to 8 per cent of water, depending on the time of settling, temperature, nature of the tar, and

other factors. Water-gas tar may retain 40 per cent or more water.

One kind of apparatus used for the continuous separation of tar is the baffle-plate separator, illustrated by figure 3.

The tar and water are admitted at *a* and the speed of flow is so regulated that the effluent at

*c* is water free from tar and the effluent at *b* is tar with some retained water.

A method by which tar can be almost completely freed from water, although at great expense, consists in spraying the tar over heated surfaces in a vacuum. The vapors are condensed and the small amount of light oil driven off with the water is recovered. By this process, it is claimed<sup>4</sup> the water content in tar can be reduced to less than 0.5 per cent.

Tars with specific gravities approaching that of water can not be separated from the retained water by settling, but can be successfully freed by the centrifugal method, whereby the water content can be reduced to less than 1 per cent. The centrifuge is operated at a speed of 3,000 to 17,000 revolutions per minute. This method is best adapted for the dehydration of water-gas tar.

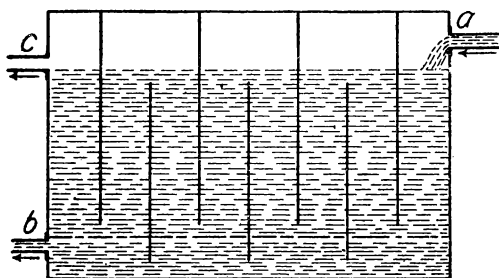


FIGURE 3.—Baffle-plate tar separator: *a*, Tar and water inlets; *b*, tar offtake; *c*, water overflow.

<sup>4</sup> Perry, R. P., Tar distillation in the United States, general development and recent progress: 8th International Congress of Applied Chemistry, vol. 10, 1912, p. 242.



Centrifuging removes part of the free carbon which adheres to the wall of the separator (centrifuge) and must be periodically removed.

In the Feld system of fractional separation the dehydrated tar products are separated directly from the gas by cooling and condensing. The process provides a progressive cooling and washing of the gas, with a progressive drop in temperature whereby the heat of the gas is utilized for separating the various tar products.

#### OPERATION AND CONTROL.

Tar is distilled in order to obtain more useful and valuable products. In determining what fractions of distillation are to be separated or where to make the "cut," it is necessary to know the relative value of the different fractions, the market conditions, and just how much or how little can be included in a particular fraction that is made for a special purpose or to meet a given specification. Such determination is not as difficult as it may seem, for the primary fractions customarily separated are not very numerous and the specifications for many of them are not so exacting but that they leave considerable leeway for the distiller. The value of, and demand for, the several fractions vary in different parts of the country, and it is natural in separating the most valuable fractions (to meet specifications) to include in them all the distillate that the specifications will permit. Distillers have often found that some one or more of the products of distillation is not readily salable. This lack of demand has been one of the pressing causes for investigation into the various uses for tar products, and into the possibility of changing the nature of such products by chemical or other means, in order to obtain more valuable and more salable materials. That the net result of all the studies of tar and its products was a great success is shown by the large number of intermediate and finished products derived from tar that are on the market.

#### ONE METHOD OF DISTILLATION.

One method of distilling and separating fractions is as follows: After the still is filled from one-half to two-thirds full with warm settled tar, and all the cocks are closed, only the main offtake being open, a fire is started in the furnace beneath the still. This fire is not forced but—quite the contrary—a heavy fire is avoided at this stage. As the tar heats, water is vaporized and condenses in the condenser. With this water is a small amount of a very light (low specific gravity) oil which is usually called crude naphtha, but in some works it is termed crude benzol. The mixture of oil and water continues to come over until all the water has been distilled, the fraction containing considerably more water than oil unless the tar has

been dehydrated previous to distillation. This mixture—oil and water—is referred to as “first runnings.” The more water there is in the tar, the greater is the tendency of the liquid to froth and boil over and the greater the necessity of keeping the fire low and under perfect control. As the distillation of this fraction proceeds, the proportion of water in the distillate decreases and the proportion of oil increases.

After the first runnings are “over,” that is, when water no longer appears in the distillate, a “change” is made and the oil coming over is run into another container reserved for “light oil.” When this change is made the oil, which usually has a light lemon color and is clear, runs more smoothly from the condenser in a steady stream. The specific gravity of the oil coming over at the time the first change is made is approximately 0.965, but sometimes the change made is at 0.950 specific gravity and just before the water has all distilled over. The mean specific gravity of the first fraction, “crude naphtha,” is 0.905 to 0.920 at 60° F., varying with different tars. The distillate coming over as the second or light oil fraction has a specific gravity lower than 1.00 at 60° F. In fact, the second change is not usually made until the oil coming over has a specific gravity of 1.00 at 60° F. The mean specific gravity of the light oil is between 0.960 and 1.00, these being the specific gravity limits between which the light oil is usually separated, and is not much more or less than 0.985.

An oil heavier than water is collected after the second change is made, when the oil coming over has a specific gravity equal to 1.00 at 60° F. This is called carbolic oil, as it contains most of the carbolic acid that distills over, its odor is sharper and more penetrating than that of the lighter fractions, and its color is a deep yellow or light amber. It is collected as carbolic oil until its specific gravity reaches 1.025, or sometimes 1.03, at 60° F. The specific gravity of the whole fraction is close to 1.015. Considerable solid matter usually crystallizes on cooling and standing. The solid matter, chiefly naphthalene, is yellow and rather granular and loose as it first forms, but on slow cooling or long standing the mass frequently has the appearance of brittle wax. This fraction as a whole can be pumped before it has stood too long or has become too cold; in the latter event it must first be heated, preferably with a steam coil.

As solid matter crystallizes from this fraction on cooling, the water in the condenser must be allowed to become warmer in order to avoid “plugging” or “choking.” This warming is accomplished by merely decreasing the supply of feed water to the condenser.

The next or fourth fraction to come over is called “creosote,” “dead oil,” or “heavy oil,” and is usually the last fraction separated. It is not always the last fraction, however, for sometimes an anthracene fraction, otherwise included in the creosote, is collected.

The properties of "creosote" depend largely on the completeness of the distillation. When soft pitch is desired as a residue from distillation, the volume of creosote will be smaller and there will be usually but a small amount of solid matter crystallizing from it at ordinary room temperature ( $60^{\circ}$  to  $70^{\circ}$  F.). If hard pitch is made, the volume of this last fraction is greater, as the distillation is carried further, the distillate coming over during this later stage being chiefly solid at  $60^{\circ}$  F.; hence the proportion of solids in the creosote is greater when the distillation is carried to a hard pitch. The color

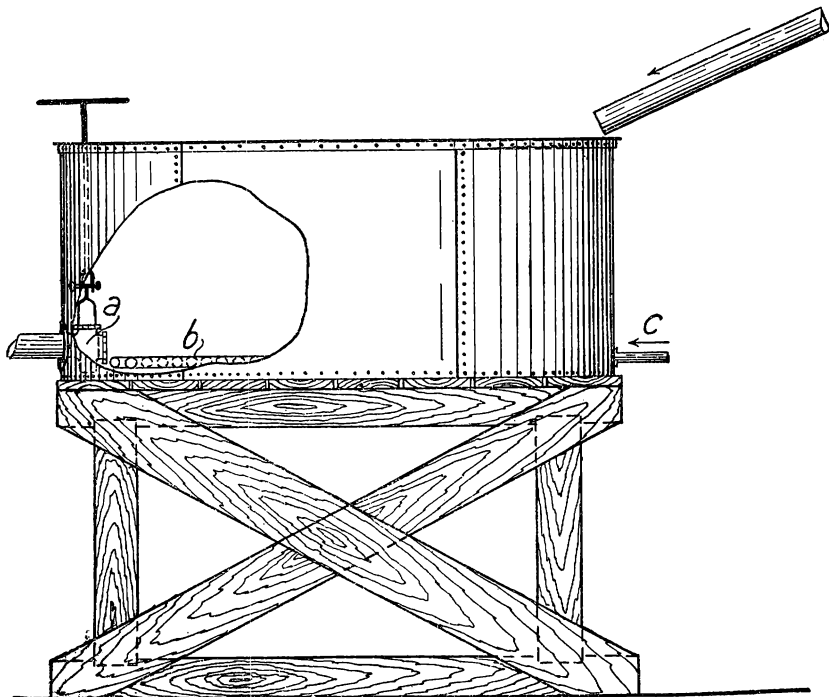


FIGURE 4.—Pitch-cooling tank used in small plants: *a*, Draw-off valve; *b*, steam coil; *c*, steam inlet to coil.

of the first part of the creosote fraction is amber, gradually changing as distillation proceeds to a dark amber or amber red. The solid part, if collected separately, is greenish brown or olive and greasy.

The residue in the still—pitch—is drawn off and then cooled in a cooling tank (see fig. 4) to a temperature suitable for barreling. This tank is covered to keep out rain and snow and has a steam coil for heating the pitch, in case it should become too cold before barreling. The pitch is then drawn off into tight, dry, open-headed barrels, in which it solidifies on further cooling and in which it is usually shipped. In the larger plants, however, where a very hard

grade of pitch is made, the latter is generally drawn off into a specially provided pool in the open air where it is stored.

When a distillation is made to a soft or a medium pitch and the fractions separated as described the following yield may be anticipated:

Coal tar:

	Per cent by volume.
1. First runnings—	
Water-----	1 to 5
Crude naphtha-----	1 to 2
2. Light oil-----	1 to 4
3. Carbolic oil (middle oil)-----	5 to 10
4. Creosote oil (heavy oil)-----	10 to 22
5. Pitch-----	60 to 80
6. Uncondensed gases and other losses-----	1 to 2
Total-----	100

In the figures for the yield of oils just given, no deductions are made for solids that crystallize out on cooling.

The change in properties of the fractions on distillation proceeds gradually. There is no sharp mark of distinction between the oil that comes over at the end of one fraction and that which comes over at the beginning of the next. The number of fractions or "cuts" to make is determined by the distiller, who, in order to sell his products, must be guided by the demands or requirements of his customers. If the raw distillates are to be utilized in the preparation of manufactured products at the distillery, that portion of a distillate best suited for a given purpose is separated as a distinct fraction. If, for example, there is no particular use or market for carbolic oil, but there is a demand for creosote or oil heavier than carbolic, it may be possible to sell the total heavy oil collected as one fraction and thus eliminate the necessity of separating and storing a middle oil fraction. Other similar considerations arise in the operation of a tar distillery and the cuts are made in accord with prevailing conditions.

#### THERMOMETERS AND PYROMETERS.

When distillations or analyses are made in a chemical laboratory, the fractions are separated according to the temperature of the vapors leaving the retort or still. This is also the proper way to make cuts of a distillation in a plant still, but it is not employed in many of the smaller plants and in fact is not necessary.

Practically all stills are equipped with thermometers, which are used when tar is first distilled and when special fractions are separated. However, when only one kind of tar is used the operator soon finds that the volume, color, and smell of the distillate show him when to make a change. If the distillations are all of one given tar under

approximately the same conditions, the volumes of the different fractions do not vary from one distillation to another. The chemist, distilling tar in laboratory flasks, knows between what temperature limits a given compound or class of compounds will come over. He can, therefore, define the temperature limits between which any or all the fractions will distill if he knows what the fractions are to be used for or what their specifications are. In plants where the fractions are separated in various ways and where many different tars are distilled it is essential that the operation of the still be governed by laboratory tests. Such tests will avoid many mistakes and perhaps some accidents.

It has been demonstrated by such tests and by actual works tests that some coal tars may be distilled, with the temperature as a guide, the fractions separating as follows:

1. Crude naphtha and water.....	}	° To 210° C.
2. Light oil.....		
3. Carbolie oil.....		210° C. to 240° C.
4. Creosote oil.....		240° C. to 270° C.
5. Anthracene oil.....		Above 270° C.

The final end point where the distillation should be stopped can not be foretold in a way that will apply exactly to all tars, the point being determined by the quality of hard or soft pitch that is desired. For a medium grade of pitch, such as is used by roofers, the firing is stopped when the odor, which is noticeably different toward the end of the "run," is more pungent and like ammonia. The heat of the brickwork will carry on the distillation, though slowly, for one-half hour to one hour. The specific gravity of the oil coming over last is usually 1.10; but when hard pitch is made, the specific gravity is 1.14. A satisfactory way of ascertaining the correct end point is to distill a small quantity of the tar in a laboratory still, observing the change in properties, odor, and color of the oil toward the end of the run, the total volume of distillate, the properties of the pitch residue, and the temperature. After an operator has made a number of distillations of a given tar he can determine the end point and end the distillations uniformly.

Another guide in determining the end for the distillation is a sample of the pitch remaining in the still. When a sample of this pitch is drawn it should be cooled as rapidly as possible to prevent excessive loss of vapors from its surface. Care should be taken to avoid the sticking of the valve through which the sample is drawn, for if a large quantity of hot pitch is let out in contact with air it is apt to take fire spontaneously.

<sup>5</sup> Centigrade and Fahrenheit degrees are referred to frequently in this paper, since both are used commercially. A method converting one to the other follows:

Degrees Centigrade= $5/9$  (Fahrenheit temperature-32).

Fahrenheit temperature= $9/5$  (Centigrade temp.) + 32.

0° C.=32° F. and 100° C.=212° F.

When hard pitch is made by mistake, it is frequently "cut back" by adding to it in the pitch tank enough of the last fraction removed by distillation to give a soft or medium pitch, as desired. When the distillation has not been carried too far, "cutting back" can be done without seriously affecting the quality of the resulting pitch, but the practice is objectionable and should be avoided when possible. If the distillation has been carried too far, "cutting back" will not remedy the error and a good quality of pitch can not be made. In fact, if the distillation is continued until the residue is a honeycombed carbonaceous mass, pitch can no longer be made from it; the residue—coke—will have to be chopped out of the still.

#### USE OF SUPERHEATED STEAM.

During the last stage of distillation the vapors formed in the still are very heavy and have a decided tendency to condense and fall back into the distilling tar or pitch. The more this takes place the greater is the tendency for the heavy hydrocarbons to "split up," crack, or decompose into lighter hydrocarbons and carbon. Thus the pitch may be expected to contain more free carbon than that originally present in the tar. In order to hasten this part of the distillation without increasing the temperature unduly and without forcing the fire, superheated steam is generally used in large works. By using steam the fire can be withdrawn earlier and there is not so much heat stored in the bricks at the end of the distillation; the danger of damage to the still and the tendency of hydrocarbons to "crack" and increase the carbon content of the pitch are both decreased, and the distillation can be more quickly terminated. The net result is better control of the quality of the pitch residue.

The superheated steam for this purpose is admitted to the contents of the still in small jets, which play against the bottom or the part of the wall exposed most to the action of heat. It is first blown in (for finishing the distillation) toward the end of the creosote fraction or when the temperature recorded is 270° C. Steam that is under 50 to 60 pounds of pressure and superheated to 275° C. is satisfactory. The greater the total heat of the steam, the less of it is required to distill a given amount of oil. .

Both air and inert gases have been utilized to aid the distillation of tar; in addition, they have been used with steam. As use of the three at one plant is not common practice in this country it will not be discussed here. In large plants in the United States air is sometimes used with steam during the latter part of the distillation and the free-carbon content of the resulting pitch is said to be reduced 4 to 5 per cent. The volume of air used is slightly less than 30 cubic feet per gallon of tar distilled.

A vacuum method, involving evaporation under reduced pressure, has been successfully used in the distillation of tar. This is described in "Coal tar and ammonia," by George Lunge.<sup>6</sup> Some of the advantages of this process are:

1. Distillation can be made more rapidly.
2. Heavy vapors have practically no tendency to condense within the still and fall back into the distilling liquid.
3. The danger of clogging the offtake pipe is practically eliminated.
4. The loss of ammonia and condensable tar vapors is decreased.
5. The quality of the distillates is said to be improved.

### SPECIFIC GRAVITY.

Crude tar distillates are often judged by the specific gravity test. Moreover, the different fractions formed by distillation are usually separated as the specific gravity of the oil changes. It is necessary to make use of specific gravity tests so frequently that a definition of the meaning of the term is perhaps warranted here.

Specific gravity is the ratio of the weight of any volume of one substance to the weight of an equal volume of another substance taken as standard, both substances weighed under the same conditions. As water is the standard commonly used for liquids and solids, its specific gravity is 1.0. If a container with a capacity of 2 pounds of water is filled with oil and the oil weighs 2.25 pounds, the specific gravity of the oil would be  $\frac{2.25}{2.00} = 1.125$ . In other words, the oil is approximately  $1\frac{1}{8}$  times as heavy as water.

When the specific gravity of a substance is known, the weight of any given volume can be quickly calculated, and when the weight of a known volume is given it is a simple calculation to find its specific gravity. The weight in pounds of any known volume of a substance is roughly equal to the product of 8.33 times the volume in cubic feet times the specific gravity times 7.48. The figure 8.33 represents the approximate weight of 1 gallon of water under standard conditions, and there are 7.4805 such United States gallons in a cubic foot. These figures and calculations involving them are in frequent use by the tar distiller.

In order to avoid the necessity of weighing liquids and calculating the specific gravity therefrom, the hydrometer is universally used. This is an especially prepared float comprising a hollow glass instrument (see fig. 5, p. 23) with graduations on the narrow stem reading in terms of specific gravity or the equivalent degrees Baumé. The principle of the hydrometer is that a floating body rides higher in a heavy liquid than in a lighter one. In using this instrument, it is

<sup>6</sup> Lunge, George, Coal tar and ammonia. London. 1916, vol. 1, p. 464.

desirable to have the eye on a level with the surface of the liquid when the reading is taken.

Such instruments as are used in a tar distillery are generally based on the specific gravity of water being equal to 1.0 at 60° F. (15.6° C.).

Table 3 shows the relation of the different hydrometer readings for heavy liquids and for liquids lighter than water.

TABLE 3.—*Equivalent Baumé degrees and specific gravity at 60° F. (15.6° C.).*

For liquids heavier than water.		For liquids lighter than water.	
Specific gravity.	Degrees Baumé.	Specific gravity.	Degrees Baumé.
1.00	0.0	1.00	10.0
1.01	1.4	.99	11.4
1.02	2.8	.98	12.9
1.03	4.2	.97	14.3
1.04	5.6	.96	15.8
1.05	6.9	.95	17.4
1.06	8.2	.94	18.9
1.07	9.5	.93	20.5
1.08	10.7	.92	22.2
1.09	12.0	.91	23.85
1.10	13.2	.90	25.55
1.11	14.4	.89	27.3
1.12	15.5	.88	29.1
1.13	16.7	.87	30.9
1.14	17.8	.86	32.8
1.15	18.9	.85	34.7
1.16	20.0	.84	36.7
1.17	21.1	.83	38.7
1.18	22.1	.82	40.7
1.19	23.15	.81	42.8
1.20	24.20	.80	45.0
1.21	25.2	.79	47.2
1.22	26.15	.78	49.5
1.23	27.1	.77	51.8
1.24	28.1	.76	54.2
1.25	29.0	.75	56.7
1.26	29.9	.74	59.2
1.27	30.8	.73	61.8
1.28	31.7	.72	64.45
1.29	32.6	.71	67.2
1.30	33.5	.70	70.0

It is important that the temperature at which the specific gravity is taken should be noted and necessary corrections made. Occasionally, the specific gravity at 60° F. is desired of a product that is not entirely liquid at that temperature, or a determination must be made rapidly and at a higher temperature, as at the still, in which event allowance must be made for the expansion—increased volume—of the oil at the higher temperature. A similar correction must be made, in the opposite direction, when the determination is made at temperatures lower than standard (60° F. or 15.6° C.). The correction for each degree above or below this temperature is 0.0008 for each degree centigrade and 0.00044 for each degree Fahrenheit. The total correction is to be added to the observed reading when taken at temperatures higher than 15.6° C. (60° F.) and subtracted when taken at temperatures lower than 15.6° C. (60° F.). Thus, if the hydrometer reading at 85° F. (25 degrees above 60° F.) is 1.06, the true



specific gravity at 60° F. is  $1.06 + (25 \times 0.00044)$  or  $1.06 + 0.01100 = 1.071$ . These correction factors are taken from Church,<sup>7</sup> and are for tar distillates only, as other oils have different factors, and although not absolutely exact, it seems to be as reliable a figure as any that can be applied to tar oils generally.

## USES OF TAR AND ITS SIMPLE DERIVATIVES.

### TAR.

Many uses have been found for raw or dehydrated coal tar. In fact, these are so numerous that there is no longer an excuse for throwing tar away or disposing of it wastefully. Some of the uses for tar and preparations in which it is employed are as follows: Timber preserving, fuel, tarred felt, paint for stone, brickwork, and iron, road-construction material and road-dust settler, waterproofing compounds for cement and for roof paint, germicides, and miscellaneous special preparations.

### TIMBER PRESERVING.

For many years coal tar has been used extensively as a timber preservative; its antiseptic and preserving properties are recognized throughout the world. Tar prevents decay not only by its antiseptic properties but also by its waterproofing qualities, whereby the pores of the wood are filled. It is used to preserve fence posts, telephone poles, and heavy building timbers, and for such purposes is applied with a brush or the timbers are dipped in hot water-free tar. By far the largest proportion of the tar used for preserving timber, however, is mixed with creosote oil. Large quantities of mixtures of this nature are used annually to treat paving blocks, railroad ties, crossarms, and telephone poles. The brush method is not as common for this purpose as the closed-tank pressure method, wherein the actual absorption of the preservative is many times greater. Although it is generally understood that some of the tar distillates are superior to tar for preserving timber (especially when the proportion of free carbon in the tar is high), the difference in first cost favors tar.

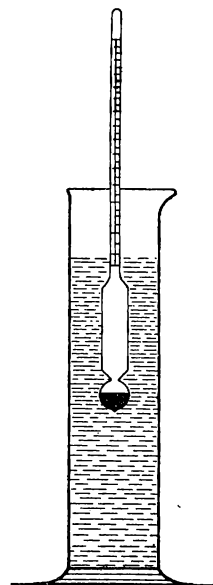


FIGURE 5.—Hydrometer method of determining specific gravity.

<sup>7</sup> Church, S. R., Methods for testing coal tar and refined tars, oils, and pitches derived therefrom: Jour. Ind. and Eng. Chem., vol. 3, 1911, p. 232.

When used for treating timber the tar should be hot and free from water, and to obtain the best results the timber treated should be as dry as possible, as the absorption and penetration is considerably greater under these conditions than when the wood is wet or moist. The penetration into the wood is not so great with tars with a high content of free carbon as with those of a low free-carbon content.

The amount of preservative required per unit of area with the brush method is greater for tar than for tar distillates. The exact amount can not be stated by a figure universally applicable, because the condition and kind of wood, as well as the quality and kind of tar, affect the results. However, it can be said that a gallon of hot tar will cover approximately 200 square feet of the surface of smooth, dry poles. More tar is absorbed by dry, rough-sawed timber, and a gallon of hot tar will cover 150 to 200 square feet of such surface.

#### FUEL.

Although the high heating value of tar has long been recognized, it is only in recent years that tar has been successfully utilized as fuel, partly because of a lack of understanding of the nature of the conditions under which tar can be burned satisfactorily. These conditions have been thoroughly studied<sup>8</sup> not only with reference to the best type of burner but to the efficiencies of operation obtainable with different burners.

The combustion space required, draft, and other factors affecting the burning of tar as fuel have likewise been investigated, and the results have had important bearing on the utilization by combustion of tar and tarlike substances.<sup>9</sup> The heats of combustion of coal, tar, and fuel oil, expressed in B. t. u. per pound of fuel are:

	B. t. u.
Bituminous coal as received.....	10, 000 to 14, 000
Tar (coal-gas and water-gas tar) water free.....	16, 000 to 17, 500
Fuel oil .....	17, 000 to 20, 000

Although the heating value of tar is lower per pound than that of fuel oil, it must be remembered that these substances are sold by the

<sup>8</sup> Best, W. N., *The science of burning liquid fuel*: New York, 1901, 159 pp.; Peabody, E. H., *Oil fuel*: San Francisco, 1916, 134 pp.

<sup>9</sup> Kreisinger, Henry, *The significance of drafts in steam-boiler practice*: Bull. 21, Bureau of Mines, 1911, 64 pp.; Kreisinger, Henry, *The transmission of heat into steam boilers*: Bull. 18, Bureau of Mines, 1912, 180 pp.; Flagg, S. B., Cook, G. C., and Fieldner, A. C., *Experiments with furnaces for hand-fired return tubular boiler*: Tech. Paper 34, Bureau of Mines, 1914, 32 pp.; Clement, J. K., Frazer, J. C. W., and Augustine, C. E., *Factors governing the combustion of coal in boiler furnaces*: Tech. Paper 63, Bureau of Mines, 1914, 46 pp.; Kreisinger, Henry, Ovitz, F. K., and Augustine, C. E., *Combustion in the fuel bed of hand-fired furnaces*: Tech. Paper 137, Bureau of Mines, 1916, 76 pp.; Kreisinger, Henry, Augustine, C. E., and Ovitz, F. K., *Combustion of coal and design of furnaces*: Bull. 135, Bureau of Mines, 1917, 140 pp.; Wadsworth, J. N., *Efficiency in the use of oil fuel, a handbook for boiler plant and locomotive engineers*: Bureau of Mines, 1919, 86 pp.

gallon and not by weight. The heats of combustion per gallon of the two liquid fuels are as follows:

Tar  $9\frac{1}{2} \times 17,000 = 161,500$  B. t. u. per gallon.

Fuel oil  $7\frac{1}{2} \times 19,000 = 142,500$  B. t. u. per gallon.

If the heats of combustion of the three fuels were the only means of judging the economy in the use of one as compared with the others, the values might be expressed as follows:

*Heat of combustion in \$100 worth of fuel.*

	B. t. u.
Coal of 12,000 B. t. u., at \$4 per ton-----	6, 000, 000
Oil of 19,000 B. t. u., per pound, $7\frac{1}{2}$ pounds per gallon, at 5 cents per gallon-----	2, 850, 000
Tar of 17,000 B. t. u., per pound, $9\frac{1}{2}$ pounds per gallon, at 4 cents per gallon-----	4, 037, 500

However, the heating value of the fuels can not be taken as a guide for computing actual fuel costs, because the liquid fuels are burned to complete combustion with a smaller excess of air than is possible with bituminous coal. This fact allows a greater saving to be made than is apparent by comparing the relative heating values.

#### ADVANTAGES OF TAR FUEL.

Further advantages of using tar fuel are given below:

There are no ashes to be carted away.

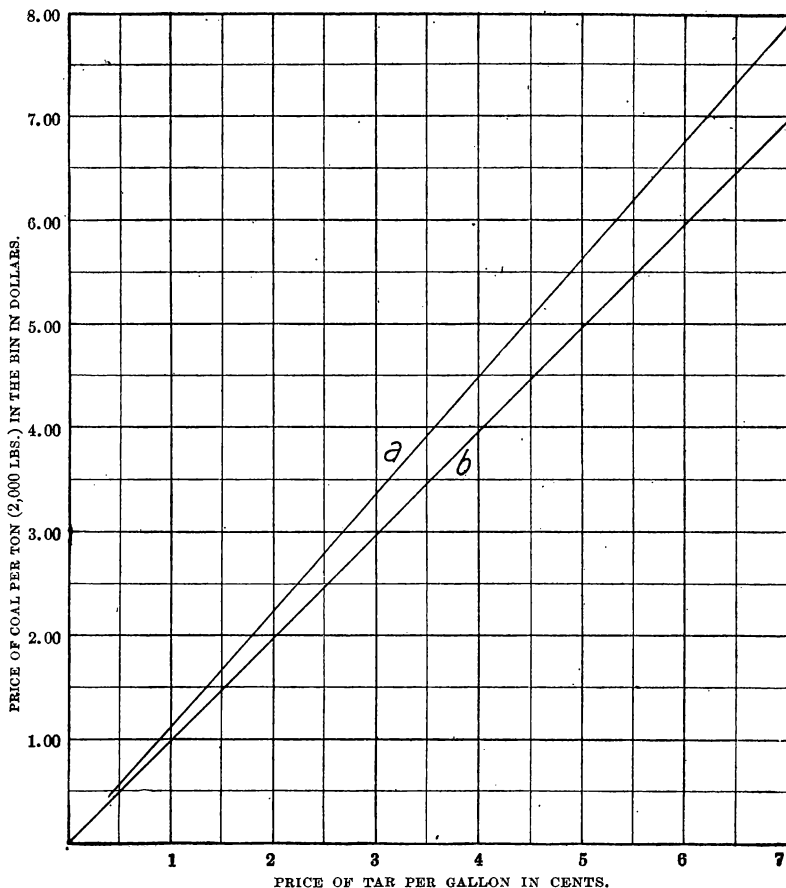
Tar as boiler fuel permits better maintenance of control over the rate of generation of steam. The fire can be started or stopped instantly. Smoke difficulties that so often prevail with bituminous coal as fuel are eliminated or reduced to a minimum.

When the tar is consumed at the plant where it is produced less fuel-storage space is required.

Less boiler-room labor is required.

If 100 gallons of tar of 17,000 B. t. u. per pound be considered equivalent, in actual operation, to 1 ton (2,000 pounds) of bituminous coal having a heating value of 12,000 B. t. u. per pound, the relative value of the two fuels at different prices can be quickly determined by referring to figure 6. This figure makes no allowance for savings that are possible by lower expenditures for labor and storage. As tar and its distillation products can be utilized for fuel, it is evident that any distillation fraction produced at the distillery for which there is no market can be disposed of to advantage. Here is an example: Assume that a gas plant producing both water-gas tar and coal-gas tar finds that it can not sell its water-gas tar but can sell its coal tar at a low price. Also assume that when the coal tar is distilled there is a good market for some of the distillates, creosote and naphtha, for instance, but no market for pitch or the other fractions. Under such circumstances the coal tar could be dis-

tilled, the crude naphtha and creosote recovered, and the other distillates and pitch mixed with the water-gas tar and the resulting tarry mixture burned as fuel. The income from selling the distillates must, of course, more than pay for the cost of distilling the coal tar.



a, Heat of combustion per pound of tar=15000 B. t. u.  
 b, Heat of combustion per pound of tar=17000 B. t. u.

FIGURE 6.—Relative value of coal tar and coal as boiler fuel, for tar with heats of combustion equal to 15,000 and 17,000 B. t. u. per lb. and  $9\frac{1}{2}$  lb. per gal., and for coal with heats of combustion equal to 12,000 B. t. u. per lb. No allowance is made for the difference in labor requirements, such as carting ashes or tending the boiler.

In burning tar the right kind of burner or nozzle should be used. Although a "home-made" burner devised by the fireman or engineer on the job may prove a success, such a burner is apt to be a failure. The writer believes that it is advisable to use a burner made and sold for use with heavy liquid fuel, one known to give satisfactory results.

The essential requirements for the successful utilization of tar as fuel are as follows:

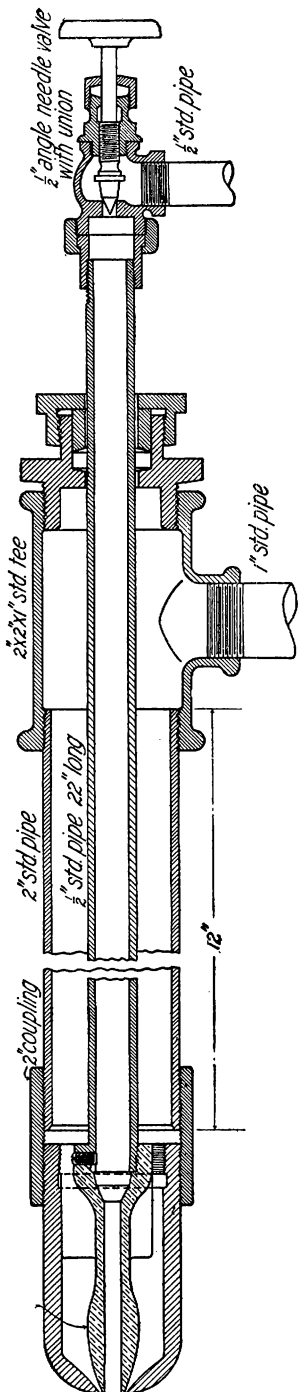


FIGURE 8.—Steese tar burner.

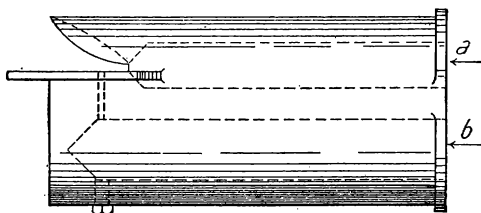


FIGURE 7.—Oil burner suitable for burning tar :  
a, Steam ; b, tar.

1. The tar must be injected into the fire box as a thoroughly atomized spray.
2. It should be strained and be free from particles that may clog the burner.
3. It must be warm enough to flow freely.
4. Air ports must be provided for supplying enough air to burn the tar completely.
5. The burner should be so designed that the fuel can not carbonize over and choke the atomizer slot; that the burner can be cleaned quickly without being removed and regulated quickly for different rates of fuel consumption.
6. When steam is the atomizing agent, provision should be made whereby only dry steam enters the burner.

Figures 7 and 8 show burners that are suitable for burning tar and have been used successfully with steam as the atomizing agent. Many other burners designed for liquid fuel are perhaps equally suitable for this purpose. Publications already mentioned in this paper contain detailed descriptions of them and their adaptability to different purposes.

#### TARRED FELT OR ROOFING FELT.

One of the early uses to which coal tar was put industrially was in the manufacture of roofing materials. Originally single sheets of millboard were coated with tar and painted with it after they were laid on the roof. Then came the treatment of large rolls of roofing

felt, which eliminated the transverse joints on the roof. The present method consists in treating special felt paper with hot tar, and removing the excess of tar by passing the felt between heated steel rollers; from the rollers the felt is run on a spindle and made up into rolls containing 250 or 500 square feet. The rolls are then wrapped in paper and are ready for the market. It is often necessary to "age" and "turn" the finished product before marketing; that is, the paper rolls are stood on end and are turned, end for end, every few days for two or three weeks, in order to keep the paper at one end of a roll from becoming "soggy." Aging and turning are necessary because the paper sometimes has more tar on it than it can absorb at once. The use of heavy cold tar also aggravates the tendency

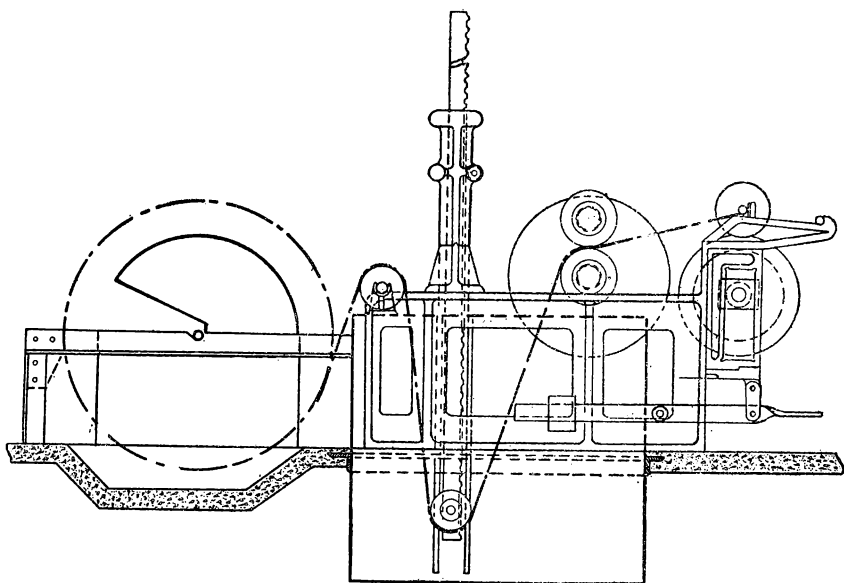


FIGURE 9.—Machine for saturating roofing felt.

of the paper to become soggy. Tar paper should always be stood on end when stored.

One form of apparatus for treating felt is shown in figure 9. The raw felt, which is supplied in rolls varying in quality and thickness and weighing from 250 to 650 pounds, is suspended on a spindle from which it unrolls as fast as it is drawn through the hot tar.

The temperature, water content, and consistency of the tar used are of considerable importance in the manufacture of a good roofing felt. While the paper is being treated with tar it is under considerable tension, because the force required to unroll it, draw it through the tar, and roll it, is exerted at one end. If the tar contains water this is absorbed by the paper, which can not now withstand the stress

and breaks or tears at the surface of the tar; consequently the tar must be free from water. Even if the paper did not break under these conditions, it is desirable that the tar should be freed of water before the felt is saturated, as the presence of water causes uneven saturation and impairs the waterproofness of the product. In order to insure a high saturation, the tar should be hot enough to reduce its viscosity and give it the consistence of a thin sirup. The limiting temperatures for the best results are 200° and 260° F.

The tar used for this purpose is sometimes prepared by distillation to a pitch and "cutting back" the pitch so obtained with creosote, or with creosote and light oil, and is called "prepared tar." It is preferable, as a rule, to use "straight" dehydrated tar, thinned, when necessary, with light oil or creosote that has been cooled and freed from naphthalene. When the natural tar is so high in naphthalene that the desired saturation can not be obtained without the naphthalene causing the layers of tarred felt in a roll to stick together, the "prepared tar" is preferable. Usually naphthalene is not present in such proportions, particularly not in "straight" coal tar.

Felt absorbs from 100 to 200 per cent of its weight of tar. When it is oversaturated, or when the excess of tar has not been removed by the rollers, the sticking of the convolutions of the tarred felt in a roll may make unrolling difficult or even impossible. If the felt is undersaturated, the finished product will be porous, capable of absorbing moisture, and therefore less waterproof. The degree of saturation is controlled by the time the felt is allowed to remain in contact with the tar, which may be governed by the depth of immersion, and the speed of travel through the tar.

The steam-heated rolls between which the felt passes (see fig. 9) prevent the paper from cooling too quickly, aid the absorption of the surface tar, and remove the excess tar. Saturated felt so prepared is employed chiefly for pitch and gravel roofs or as a basis for slate and tile roofs. It is sometimes used as building paper and as deadening felt and for waterproofing walls, tanks, and tunnels, where it is applied as on a roof.

A number of kinds of tarred roofing papers, differing mainly in degree of saturation and weight per square foot, are on the market. Soft thick felts absorb more tar per square foot than thin hard felts, and a roll of tarred soft felt is therefore heavier than a similar sized roll of tarred hard felt. Some of the more common saturated felts in general use are slaters' felt, made in two grades, weighing 30 and 40 pounds, respectively, per 500 square feet; and tarred felt, made in three grades, weighing, respectively, 60, 70, and 75 pounds per 500 square feet.

Heavier felts than these are made but are not in as wide demand.

## PAINT FOR STONWORK, BRICKWORK, AND IRON.

As an inexpensive coating for brick or stone work exposed to the action of acid vapors, alkalis, or the atmosphere, tar is a ready and satisfactory material. Although tar dries more slowly than some specially prepared pitch paints, it is used extensively as a paint. It should be dehydrated, and is usually applied hot.

Hot water-free tar is also used for painting underground iron pipes and for coating castings, pipe fittings, and metal roofs that are exposed to the atmosphere. It is not so resistive to the weather as specially prepared pitch paints (see p. 4), but it is a good preservative and answers the purpose well where an inexpensive coating must be used.

## ROAD-CONSTRUCTION MATERIAL.

Tars and tar products are fast replacing mineral-oil products for surfacing roads. This fact may be variously ascribed to the increasing supply of suitable tars, the decreasing supply of suitable mineral-oil products, increased appreciation and recognition of the suitability of tars, and the more general availability of tars in practically all parts of the country.

Lunge<sup>10</sup> reports that in Great Britain in 1907 there were only 100 miles of road covered with tar or tarry mixtures, whereas in 1908 there were 700 miles; in 1909, 3,000 miles; and in 1910, 7,000 miles of such road.

A number of specifications have been drawn up for the tar to be used for this purpose, a fact not at all surprising in view of tars being produced under so many different conditions, and the roadbed, surfacing materials, and traffic and climatic conditions differing widely from place to place. Road tars are used for various purposes, and may be applied in different ways to obtain a particular result—a further cause for the wide variance in specifications. They may be used as a binder in place of cement, as in bituminous macadam roads, for dust-settling purposes or for cementing material—grouting—in the construction of brick, stone, or wood-block pavements. Although the material used for these purposes is usually either a soft pitch or a refined tar, or a mixture of the two, it is quite generally termed “road tar.”

A bituminous material such as tar and pitch is used on gravel and crushed-stone roads in several ways: First, it may be forced into the interstices between the stone after it is placed on the road; second, it may be thoroughly mixed with the stone or gravel before the latter is placed on the road (care being taken to avoid using an excess of it); and third, it may be applied to the surface of a finished gravel

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<sup>10</sup> Lunge, George, Coal tar and ammonia. London. 1916, 739 pp.



or broken-stone road with or without a final topping of coarse sand or fine gravel. The pavement produced by the first method cited is called bituminous macadam; that produced by the second method is known as bituminous concrete.

#### BITUMINOUS MACADAM.

On a subgrade, prepared by the usual method of grading, draining, and rolling, a base, or bottom course, of broken stone (1 to  $3\frac{1}{2}$  inch) is laid; after this has been rolled, a second course of broken stone, usually of somewhat smaller (1 to  $1\frac{1}{2}$  inch) size, is laid on top of it. The prepared "road tar" or pitch is forced into the interstices of the top layer, which is then covered with finely cut, one-fourth to three-fourths inch stone to fill all voids. After this surface is properly rolled, a final coat of similar bituminous material is applied, covered with fine gravel or screenings, and rolled. The pitch used for the top coat is softer than for the main binding material. The depth of each course is predetermined according to the kind and amount of traffic the road must bear. The binder is always applied hot— $200^{\circ}$  to  $225^{\circ}$  F.—and the amount used per square yard varies between  $1\frac{1}{4}$  and  $1\frac{3}{4}$  gallons, depending on the depth and on the size of stone. In preparing the final surface or "seal coat," one-third to three-fourths gallon of binder is used per square yard of road.

#### BITUMINOUS CONCRETE.

Bituminous concrete pavement is prepared much like concrete pavement, except that the binding material is a bituminous substance instead of Portland cement. A first course of crushed rock is put down as for bituminous macadam; on top of this is laid a layer of mixed crushed rock and sand that has been thoroughly mixed or coated with a bituminous material (pitch). This layer is applied and rolled while hot. The pavement may be left in this condition, but much of it is given a "seal coat" by spreading a layer of the bituminous material (usually thinner and of lower specific gravity than the main binder) over the surface, covering it with fine gravel or coarse sand, and rolling. The size of stone ranges from one-fourth to  $1\frac{1}{2}$  inches, according to conditions, but the custom is to use the larger sizes in the thicker pavements. One specification requires a mixture of 1 cubic yard of grit sand less than three-eighths inch and 3 cubic yards of broken stone, three-fourths to  $1\frac{1}{2}$  inches. The material must be thoroughly coated, during mixing, with the bituminous binder, and an appreciable excess of binder should be avoided. One specification requires that 18 gallons of it be used per cubic yard of stone, approximating 5 to  $7\frac{1}{2}$  per cent by weight in the finished pavement, but others require 25 to 30 gallons per cubic yard of material

treated. The mixing is always done hot at 180° to 300° F. and the mixture is delivered at about 150° F.

#### **SURFACING FOR OLD ROADS.**

When old roads are repaired, it is often the practice to apply a "blanket" or "seal" coat to the surface after the necessary repairs are made. For this purpose, a heavy refined tar or soft pitch is suitable, and the amount used per square yard ranges from one-half to 1 gallon, according to the thickness of the coat and the condition of the surface to which it is applied.

#### **ROAD PRESERVER AND DUST SETTLER.**

In the maintenance of roads, it is desirable in many places to apply periodically a thin layer of bituminous material to the surface. For this purpose, refined tar is often suitable. The tar is preferably applied hot, but sometimes is applied cold, in which event it must, of course, be thinner than a soft pitch in order to spread properly. Less than a gallon per square yard is used, and ordinarily but 0.2 gallon.

Such a coat retards the formation of dust. For this purpose, tar is superior to many of the oils that are sometimes recommended and sold as dust preventives. Prof. Agg<sup>11</sup> says that in oiling roads "there is some danger of introducing into the surface an oil that will act as a lubricant instead of as a binder, and in that event the road will become loose and rapidly develop pot holes and ruts under traffic. Considerable difficulty has been experienced throughout the United States from that source, and too much emphasis can not be put on the importance of using a good asphaltic base oil or a suitable grade of tar." It is undoubtedly true that tar has less lubricating qualities and contains a greater proportion of bitumens—binding material—and has greater antiseptic and germicidal properties than most mineral oils. Consideration of the foregoing statements will indicate how prominent tar is to be as a road material; moreover, statistics show that the yearly production of coal tar is rapidly increasing, whereas the demand for mineral oils is growing faster than the supply, with prospects of higher prices. Tar is now sold at many works at a lower price per gallon than good mineral oil (road oil).

#### **FACTORS RETARDING THE MORE EXTENSIVE USE OF ROAD TAR.**

General utilization of tar for road building and surfacing has been retarded by the promiscuous use of any and all grades of tar on all sorts of roads, without regard to climatic conditions or the

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<sup>11</sup> Agg, T. R., *The construction of roads and pavements.* New York. 1916, 432 pp.

condition of the road. Obtaining the best results requires the use of judgment. Special care should be taken that tar is not applied to wet or frozen roads and that it is hot enough to be of the consistency most suitable for the particular road treated. When tar is spread thickly, under conditions that do not permit ready absorption, it may be spattered on automobiles and other vehicles to such an extent as to cause prejudice against all tar pavements. After crossing such a street afoot, people with white shoes are not apt to have a very kindly feeling toward tar as a road-surfacing material.

The best results are obtained when the road to be treated is dry, free from dust, and warm, and the tar used is water-free and hot.

#### SPECIFICATIONS FOR ROAD TARs.

Specifications for these tars are made with the following intentions:

1. To avoid adulteration or dilution with inferior products.
2. To insure a bitumen content high enough for the purpose.
3. To reduce lubricating properties to a minimum.
4. To provide for the use of tars of the proper consistence only.
5. To avoid the use of tars that will cause rapid deterioration of the road.

As a complete discussion of the merits or defects of the various tars can not be presented here, only their principal requirements are mentioned.

The specific gravity of a pure crude tar has considerable significance to a chemist and is one of the factors governing purchase; however, as mixing very light oils with pitch will yield a tarry mixture of any intermediate specific gravity, the specific gravity alone is not a reliable test. To prohibit this "cutting back" of pitch with light oils that are volatile and undesirable in a road tar, the loss on heating a sample to a given temperature in a distillation apparatus is limited to a given maximum. The addition of mineral oils is guarded against by stating the specific gravity of the fractions obtained on distillation, or by chemical tests. The specific gravity of high-boiling fractions from the distillation of coal tar is greater than 1.00, whereas the specific gravity of mineral fractions is less than 1.00. To insure a high enough bitumen content, the percentage of distillation residue above a defined temperature and the percentage of free carbon are limited. The lubricating properties are avoided by employing only those tars that do not contain any appreciable amount of paraffin oils, namely, tars of high specific gravity—coal tars. Specifications also consider the fluidity (viscosity) of the tar at a given temperature and require that the tar be applied at the most suitable temperature.

Much has been said regarding the free carbon and the naphthalene content of road tars. Some difference of opinion exists as to the maximum amounts permissible and as to the minimum amount of free carbon that will be tolerated. It is generally agreed that a great excess of either naphthalene or carbon is detrimental, and should not be allowed. Tars with very small content of free carbon are frequently inferior to those with a moderate content. The upper limit sometimes set for the free carbon content of tars used as binder is 25 per cent and the lower limit is frequently 12 per cent. For hot surfacing the limits are 22 and 10 per cent. Sample specifications for road tars for various purposes are given in Table 4.

TABLE 4.—*Specifications for tars.*

## FOR BITUMINOUS CONCRETE.

[Standards adopted Oct. 14, 1916, by American Society of Municipal Improvements.]

Items.	Water-gas tar.	Coal tar.
1 <sup>a</sup> . Shall not foam at..... ° C.	150	150
2. Specific gravity at 25° C. (77° F.).....	1.16 to 1.20	1.20 to 1.30
3. Viscosity by New York float apparatus..... seconds.	140 to 170	140 to 170
4. Bitumen soluble in carbon bisulphide, not less than..... per cent.	95	75 to 90
5. <sup>b</sup> Distillation yield to 170° C. (338° F.) not more than..... do.	0.0	0.0
Distillation yield to 270° C. (518° F.) not more than..... do.	7.	10.
Distillation yield to 300° C. (572° F.) not more than..... do.	20.	20.
6. Distillate, total, specific gravity at 25° C.....	1.00 to 1.02	1.03
7 <sup>c</sup> . Distillation residue, melting point of, not more than.....	75° C. (167° F.)	75° C. (167° F.)

## FOR BITUMINOUS MACADAM.

[Standards adopted Oct. 12, 1916, by American Society of Municipal Improvements.]

	121° C. (250° F.)	121° C. (250° F.)
1. Shall not foam at.....	1.15 to 1.20	1.18 to 1.30
2. Specific gravity at 25° C. (77° F.).....	120 to 150	150 to 180
3. Viscosity by New York float apparatus..... seconds.	95	80 to 95
4. Bitumen soluble in carbon bisulphide, not less than..... per cent.	0.5	0.5
5. Distillation yield to 170° C. (338° F.) not more than..... do.	12.0	10.0
Distillation yield 0 to 270° C. (518° F.) not more than..... do.	25	20
Distillation yield 0 to 300° C. (572° F.) not more than..... do.	0.98 to 1.02	1.02
6. Distillate, total, specific gravity.....	75° C. (167° F.)	75° C. (167° F.)
7. Melting point of residue, not more than.....		

<sup>a</sup> This test signifies that the water has been removed, as tars that contain water foam on being heated.<sup>b</sup> Distillation is made according to the 1911 tentative specifications of the Society for Testing Materials. 100 c. c. of tar is distilled in an Engler flask, the thermometer bulb being at the offtake arm.<sup>c</sup> The melting point is determined by the cube method.*Specifications for joint-filler "tar" (pitch) for wood blocks, stone, or brick.*

## Pitch, straight run from coal tar:

Specific gravity at 78° F.....	1.24 to 1.32
Melting point..... ° F.....	115 to 150
For mastic filler..... do.....	115 to 135
For brick and stone blocks..... do.....	125 to 140
For wood blocks..... do.....	140 to 150

Free carbon (per cent)..... Not less than 22 nor more than 37.

*Distillation.*—The specific gravity of the distillate at 670° F. shall not be less than 1.07 at 140° F. compared with water at that temperature. The distillation is made in an 8-ounce retort. The amount of oil distilling up to 670° F. in this method is approximately the same as distills up to 314° C. in the flask method.

## REQUISITES FOR ROAD-DUST SETTLERS.

The very light tars are most suitable for road-dust settlers. The free carbon should be very low, the lower the better, usually, and water and naphtha should be removed. Water-gas tars are good for this purpose. As the surface on which the tar is to be applied must be considered, it is evident that specifications might require anything from a crude to a highly refined or specially prepared tar. The following requirements are representative for a coke-oven tar, water-gas tar, or other tars low in free carbon:

*Specifications for light tar for road-dust settler.*

Specific gravity 25°/25° C.....	1.10 to 1.14
Specific viscosity, at 40° C.....	25 to 35
Total distillate by weight (flask distillation):	
To 170° C. not more than.....per cent..	2
Total up to 270° C. not more than.....do.....	25
Total up to 300° C. not more than.....do.....	35
Free carbon, not more than.....do.....	5

To be applied hot or cold (but preferably hot), using one-third to one-half gallon per square yard for first application and one-tenth to one-fifteenth gallon per square yard for subsequent applications.

Frequent changes in specifications have resulted from the experiments that are being carried on continually with various tar preparations. Specifications for such materials that have been used with success have been published by the U. S. Department of Agriculture.<sup>12</sup> These are not represented as "standard" but as "typical" specifications. In general a tar from which the fraction boiling below 150° to 170° C. has been distilled off makes a suitable material for a primer or surface coat on macadam, gravel, or shell roads, especially if the tar contains a rather low percentage of free carbon. High-boiling fractions are sometimes added to increase the fluidity of the product and decrease its content of free carbon. Methods of "meeting" specifications are mentioned in a later section of this paper.

When surface coats and dust preventives are applied care should always be taken to see that the road is dry and free from accumulations of dust and dirt. It is best to sweep the road clean before treating it.

## WATERPROOFING AND ROOF PAINT.

Coal tar and water-gas tar, when free from water, make excellent paint for shingle roofs, being good, of course, as black paint only; but roofs painted with these tars look rather like slate and do not retain an undesirable jet black appearance. Retarring does not have to be done as often in order to keep the roof in repair. Tar should

<sup>12</sup> Hubbard, Prévost, and Reeve, C. S., Typical specifications for bituminous road materials: Bull. 691, U. S. Dept. of Agriculture, 1918, 60 pp.

be applied when a roof is dry and preferably when it is warm, as when it is exposed to the direct rays of the sun. A greater penetration is obtained by using a tar of low free-carbon content and applying it hot or warm.

As a protective coating, or for renewing the freshness of a "patent" roof (one covered with prepared roofing paper), dehydrated tar is inexpensive. Although it can not be as highly recommended as a specially prepared pitch paint, discussed on page 46, it is much used.

Whenever a cheap paint with waterproofing qualities is required for coating cement, stone, or brick walls or the like, the color being inconsequential, tar may be suitable. It should be free from water, and if it is very viscous should preferably be applied hot. The less light oil it contains the greater is its value for this purpose.

#### GERMICIDE.

Although tar is not as widely used as a germicide as some of the products obtained from it by distillation and other means, still its value for some purposes is worth considering. Other things being equal, this germicidal property alone should give tar preference over mineral oils as a road-dust settler. It increases the value of tar as a paint for special places, as the interior of chicken houses, pens for small animals, stables, barns, and bunk houses. When mixed with tar oils it is used as a wood preserver.

#### MISCELLANEOUS USES.

Relatively small quantities of tar are consumed annually for many minor uses. It is used in special paints and varnishes, prepared cements, special waterproofing mixtures for cloth, felt, wood, and cement, patent fuels, smudge fuels for use in orchards, manufacturing gas, and special preservative preparations.

#### CRUDE DISTILLATION PRODUCTS OF TAR.

Many of the crude distillation products of tar are used raw, either alone or mixed with others. The demand for them is not relatively proportional to the production of each, therefore there is frequently a surplus of some one or more for which it is not easy to find a market. Some of these products are discussed in the order given herewith:

1. Ammonia water (ammoniacal liquor).
2. Crude naphtha.
3. Light oil.
4. Crude carbolic oil (middle oil).
5. Creosote oil.
6. Anthracene oil.
7. Pitch.

## AMMONIA.

Tar from the works often contains 3 to 10 per cent of water, but this amount is reduced to about 2 per cent on settling. The water that is taken off the top of the tar is not pure, but contains ammonia and ammonium salts, and is known as ammoniacal liquor. When heat is employed to facilitate settling and tanks used are open, much of the ammonia is expelled and lost. Ammonia is also liberated in the early stages of distillation with the remaining water and the crude naphtha. It may be recovered by proper methods of condensation. In small works the recovery of ammonia is not attempted, but in the larger distilleries recovery is common practice. The liquor recovered seldom contains more than  $2\frac{1}{2}$  to 3 per cent ammonia and often much less. No ammonia is produced in the manufacture of water gas, hence no ammonia or ammoniacal liquor accompanies water-gas tar, although the writer has found, during experiments in the use of bituminous coal as water-gas generator fuel, that ammonia is produced during the process of gas making. The liquor is not worked up at the tar works but is usually sold to an ammonia-refining company.

## CRUDE NAPHTHA.

Crude naphtha is used in shingle stains, in cheap paints for outside use, as a solvent for pitch in the preparation of metal paint and roof paint, and in the preparation of special so-called varnishes. It is an excellent solvent and could be used crude in paint or as a paint and varnish remover, except for its strong odor.

## LIGHT OIL.

Light oil is not used as much in the crude state as the other fractions are. It frequently contains naphthalene, some of which crystallizes from solution in cold weather. This fraction is used as light creosote in shingle stains, as a solvent in the preparation of roof paints and some metal paints, and as a fuel oil and as fuel in mixtures with pitch. Considerable light oil was formerly sold, mixed with heavy oils, as creosote, but when creosote is purchased in large quantities the specifications usually preclude such a mixture.

Coal tar is sometimes distilled in the usual way and the resulting pitch is "cut back" with light oils and water-gas tar and the resulting mixture used as fuel tar; thus the most valuable products are recovered, while the pitch, light oil, and any other surplus product is utilized as fuel. Refined coal tar is sometimes made similarly by "cutting back" pitch with tar oils consisting chiefly of light oil.

## CRUDE CARBOLIC OIL (MIDDLE OIL).

Middle oil contains most of the carbolic acid and a large proportion of the naphthalene originally present in the tar. On cooling the naphthalene crystallizes and is readily separated from the oil. The latter is used in the preparation of disinfectants and germicides, and is sold raw for such purposes. There is a decided difference between crude carbolic oil and crude carbolic acid, although in some parts of the country the former is being sold under the name "crude carbolic acid." The latter, which is a product extracted from the crude oil, is mentioned on page 59.

Middle oil is also used in mixtures with the heavier fractions as a wood preservative, the mixtures being sold under the name of creosote or creosote oil.

## CREOSOTE.

There is some confusion regarding the meaning of the word creosote. The definition given in Webster's dictionary is:

*a.* An oily antiseptic liquid, of a burning smoky taste, colorless when pure, but usually colored yellow or brown by impurity or exposure, obtained by the distillation of wood tar, especially that of beechwood. It is a complex mixture of various phenols and their ethers, the principal constituents being guaiacol, creosol, phlorol, and methyl creosol. *b.* A similar substance obtained from coal tar.

The definitions given for creosote oil are:

*a.* That part of the wood-tar distillate from which creosote is obtained by purification. *b.* The third main fraction in the distillation of coal tar, boiling from 230° or 240° to 270° C. It is a greenish yellow oil, heavier than water, containing phenols and other bodies.

From the last definition, creosote oil is the fraction distilling just after the carbolic oil and before the anthracene oil. As frequently used, however, the term has a broader application, including all the heavy oils distilling up to the temperature at which soft pitch remains in the still. Sometimes "creosote oil" means carbolic oil; then the true creosote oil is called heavy oil. Of late years tar has been added to creosote oil and carbolic oil, and the mixtures are sold as creosote, creosote oil, wood preservers' creosote, and paving-block oil, for treating timbers and wood blocks. It is accordingly not surprising that so-called creosote oil can be purchased having almost any specific gravity from 1.02 to 1.14.

Specifications for creosote oil differ so widely that the term frequently means a tar oil with a specific gravity greater than water and with a high boiling point. The word creosote is often used as synonymous with creosote oil.

True creosote oil, which comes over after the carbolic fraction, usually contains naphthalene that may crystallize on cooling.



Usually the naphthalene is not separated from the liquid, as the oil is mainly used in wood preserving, for which purpose a small content of naphthalene is not objectionable.

The two primary objects of treating timbers and wood blocks with creosote oil are to preserve the wood from decay caused by the action of molds and fungi, and to waterproof the wood to prevent warping and swelling.

Numerous experiments with the various tar oils as wood preservers have demonstrated clearly that the heavy fractions from the distillation of coal tar are superior to the light fractions or to mixtures of the light with the heavy. It has been shown<sup>13</sup> that the light oils boiling below 205° C. (401° F.) do not remain long in treated timber, whereas the heavy oils with a high content of anthracene oil remain almost indefinitely and preserve the wood from decay and from boring animals. Table 5 gives analyses of oils extracted from preserved wood after years of service. The fractional distillations were made in a glass distillation flask with the thermometer bulb at the side neck. The tar acids remaining after years of service amount to less than 1 per cent.

TABLE 5.—Analyses of extracted oils.

Samples.	Average service.	Creosote per cubic foot.	Distillation of extracted oil.								
			To 205° C.	205 to 245° C.	245 to 270° C.	270 to 320° C.	320 to 420° C.	Residue above 420° C.	Solid naphthalene from distillates.	Solid anthracene oil from distillates.	Tar acids. <sup>a</sup>
	<i>Yrs.</i>	<i>Lbs.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>C. c.</i>
19 cross ties.....	21.84	9.58	0.025	12.07	13.88	23.80	24.69	25.27	1.19	23.47	0.65
6 English piles.....	43.0	9.19	.46	16.92	15.31	21.06	22.77	23.04	.....	19.95	.61
6 American piles.....	20.2	15.64	.57	30.28	15.82	18.49	13.21	21.43	25.93	43.27	.....
4 paving blocks.....	23.6	15.70	.29	21.34	21.39	18.73	19.40	18.64	12.52	40.40	.52
1 paving block, poor service.....	9.0	5.77	9.62	14.41	19.27	41.74	11.23	3.40	.....	.....	.....
1 conduit pipe.....	14.0	8.74	5.08	27.23	10.46	27.68	19.03	9.93	23.17	14.28	.....
Average of 36 timbers giving good service....	24.9	11.18	.36	17.37	15.18	22.0	21.71	23.09	6.98	27.81	.50

<sup>a</sup> The results for tar acids are expressed as cubic centimeters in 100 c. c. of extracted oil, and therefore represent the percentage by volume of tar acids in the oil.

The method of applying creosote, the quantity used per cubic foot, and the grade most suitable depend on the kind and condition of wood to be treated and the use to which it is put. When the wood is merely dipped, as in the open-tank process, the loss of oil by evaporation is proportional to the temperature of the bath, to the percent-

<sup>13</sup> Alleman, Gillert, Quantity and character of creosote in well-preserved timbers: U. S. Forest Service Circular 98, 1907, 16 pp.

age of low-boiling oils present, and to the area of the exposed surface of the bath. With this method, an oil that has the minimum content of low-boiling constituents is particularly desirable; it should not contain an appreciable amount of free carbon. The wood will absorb only a small amount of oil when treated by this process, even under the best conditions; therefore an excessive proportion of high-boiling solids that may on chilling choke the pores of the wood during treatment is undesirable. Very often, however, tar of low free-carbon content is mixed with tar oils for use in this process, cost being the controlling factor.

In the closed-tank or pressure processes, considerably more creosote oil is used per cubic foot of wood treated, the amount ranging from 5 to 20 pounds in different specifications. A common requirement for paving blocks for exposed pavement is that the penetration be equivalent to 16 pounds of water-free oil per cubic foot of wood.

The oil used for this and similar purposes may be classed, first, as a pure distillate of coal tar, and, second, as mixtures of such distillates with pure water-free coal tar. A few sample specifications for such oils follow:

The city of Chicago specifies the following requirements for oil for the treatment of wood paving blocks.

#### **SPECIFICATIONS FOR OIL FOR TREATING WOOD PAVING BLOCKS.**

1. The oil shall be a distillate obtained wholly from coal tar.
2. It is required by this specification that the oil used shall be wholly a distillate oil obtained only by distillation from coal tar. No other material of any kind shall be mixed with it.
3. The oil shall contain not more than 1 per cent of matter insoluble in hot benzol and chloroform.
4. Its specific gravity at 25° shall be not less than 1.08 and not more than 1.12.
5. The oil shall be subject to a distilling test as follows:

The apparatus for distilling the creosote must consist of a stoppered glass retort having a capacity, as nearly as can be obtained, of 8 ounces up to the bend of the neck, when the bottom of the retort and the mouth of the off-take are in the same plane. The bulb of the thermometer shall be placed one-half inch above the liquid in the retort at the beginning of the distillation, and this position must be maintained throughout the operation. The condensing tube shall be attached to the retort by a tight cork joint. The distance between the thermometer and the end of the condensing tube shall be 22 inches and during the process of the distillation the tube may be heated to prevent the congealing of the distillates. The bulb of the retort and at least two inches of the neck must be covered with a shield of heavy asbestos paper during the entire process of distillation, so as to prevent heat radiation, and between the bottom of the retort and the flame of the lamp or burner two sheets of wire gauze each twenty mesh fine and at least six inches square must be placed. The flame must be protected against air currents.

The distillation shall be continuous and uniform, the heat being applied gradually. It shall be at a rate approximating one drop per second and shall take from thirty to forty minutes after the first drop of distillate passes into the receiving vessel. The distillates shall be collected in weighed bottles and all percentages determined by weight in comparison with dry oil. When one hundred grams of the oil are placed in the retort and subjected to the above test, the amount of distillate shall not exceed the following:

*Percentage of distillates from oil for wood paving blocks.*

	Per cent.
Up to 150° C.....	2
Up to 210° C.....	10
Up to 235° C.....	20
Up to 315°.....	40

The distillation of the oil shall be carried to 355° C. The residue thus obtained when cooled to 15° C. shall not be brittle, but shall be of a soft, waxy-like nature so that it can be readily indented with the finger. When a small portion of this residue is placed on white filter paper and warmed, the oil spot produced, when viewed by transmitted light, shall appear of an amber color.

6. The tar acids of the distillate from 250° C. to 315° C. must not be less than 6 per cent of this distillate (250° to 315° C.).

7. The amount of the unsaponifiable oil (by sulphuric acid and caustic soda) in the distillate from 250° C. to 315° C. must not exceed 3½ per cent of this distillate.

The following is the American Railway Engineering Association specification for creosote oil:<sup>14</sup>

TABLE 6.—*Commercial creosote-oil specifications.*

	Grade 1.	Grade 2.	Grade 3.
Distillation: <sup>a</sup>			
Below 210° C., not over.....per cent..	5	8	10
Below 235° C., not over.....do....	25	35	40
Residue above 355° C. must be soft and greater than.....do....	5	5	5
Water, not over.....do....	3	3	3
Specific gravity at 38° C., not less than.....	1.03	1.03	1.025

<sup>a</sup> Distillation results are calculated on the basis of dry oil when distilled by the method adopted by the Am. Ry. Eng. Asso. in an 8-ounce asbestos-covered retort, with standard thermometer and bulb one-half inch above the surface of the oil. Per cent here means per cent by weight.

Grade 1 is a pure product obtained from coal-gas tar or coke-oven tar, and shall be free from any tar, or from any oil or residue obtained from petroleum or any other source; it shall be completely liquid at 38° C. (100° F.) and shall be free from suspended matter. Grades 2 and 3 shall be the best obtainable grades of coal-tar creosote.

The specifications for creosote oil prepared by a committee on standard specifications for creosoted wood-block paving of the American Society of Municipal Improvements are given in Table 7.

<sup>14</sup> American Wood Preservers' Asso., Handbook on wood preserving. Baltimore. 1916, 73 pp.

TABLE 7.—*Specifications for wood-preserving oil.*

	Grade A.	Grade B.
Water.....per cent..	Not more than 3.....	Not more than 3.
Matter insoluble in benzol...do....	Not more than 3.....	Not more than 0.5.
Specific gravity at 38° C.....	1.07 to 1.12.....	Not less than 1.06.
Distillates:		
Up to 210° C.....per cent..	Not over 5.....	Not over 5.
Up to 235° C.....do....	Not over 25.....	Not over 15.
Residue above 355° C.....	If over 35 per cent shall have a float test of not over 80 seconds at 70° C.	If over 10 per cent shall have a float test of not over 50 seconds at 70° C.
Specific gravity, fraction 235 to 315° C.....	Not less than 1.02 at 38/15.5° C...	Not less than 1.02 at 38/15.5° C.
Coke residue.....per cent..	Not more than 10.....	Not more than 2.

Grade A is a coal-tar paving oil, a coal-tar product at least 65 per cent a distillate of coal-gas tar or coke-oven tar, the remainder refined or filtered coal-gas tar or coke-oven tar.

Grade B is a coal-tar distillate oil, a pure distillate of coal-gas tar or coke-oven tar.

It is to be noted that water-gas tar or products therefrom are not considered suitable for preserving wood. The advisability of including this tar or its products as a permissible preservative in mixtures of coal-tar creosote can not be discussed here, although it is mentioned later in discussing the properties of water-gas tar from bituminous coal.

Creosote oil is also used as a "flotation oil" in the flotation process for separating certain ores, notably sulphide ores, from the gangue mineral associated with them, the particles of finely ground ore being floated on a froth created by agitating the ore in water containing the flotation oil in amounts ranging from 0.3 to 3 per cent by weight of the ore treated. Agitation is accomplished by mechanical means, by aeration, or by both, and flotation by the employment of oil, oil and acid, or by mixtures of oil and tar. The acid-tar oils—carbolic oil and creosote oil—have been successfully used, as well as mixtures of 10 per cent tar with varying amounts of wood-creosote oil and coal-tar creosote oil.

Creosote oil is also used in the preparation of disinfectants, sheep dips, germicides, shingle stains, and bituminous paints. It is seldom used as fuel because there is usually a ready market for it for other purposes.

#### ANTHRACENE OIL.

Anthracene oil is the last fraction from the distillation of coal tar. A considerable part of this fraction is solid and greasy when separated by itself. It has been used abroad to make cheap lubricants and cart greases, but is not, to the writer's knowledge, used for that purpose here to any appreciable extent. The value of the high boiling fractions as wood preservatives has already been pointed out,

hence the reason for including anthracene oil with the creosote-oil fraction as a wood-preserving oil is evident. This is the chief use for this fraction in the crude state.

## PITCH.

The properties of the residue—pitch—remaining in the still after distillation is complete depends, for any given tar, on the final temperature of distillation. If the maximum temperature reached in the still is less than  $275^{\circ}$  C., the pitch is very soft; that is, its consistence is such that a piece will stick to the teeth when chewed. When the distillation is continued up to  $300^{\circ}$  C., the resulting pitch can be chewed like gum, and will not stick to the teeth. When the distillation is carried further, however, the pitch becomes harder, the residue over  $320^{\circ}$  C. usually being so hard that it crumbles when an attempt is made to chew it. The free-carbon content of the tar also has much to do with the consistence of the residue remaining above a given temperature, hence the temperature limits just given are correct for certain tars, and are used here to emphasize the effect of temperature on the properties of the residue. The exact temperature limit of a tar distillation to produce a pitch of a specified consistence can best be determined by first distilling a small quantity in the laboratory. It frequently helps, in finishing the distillation, to draw samples of the residue from the still toward the end of the run.

Pitch is recognized as a suitable material for roofing. The well-known pitch and gravel roof is approved by the laboratories of the National Board of Fire Underwriters as a fire retardant roof. Architects and engineers generally recognize its merits. Its resistance to atmospheric conditions and to moisture are of prime importance. This roof consists of several—usually three to five—layers of tarred felt cemented together by mopping hot pitch over each layer when in place. A heavy coat of pitch is applied on top of the final layer, and is immediately covered with very fine gravel, or sand and gravel. This kind of roof is suitable for so-called “flat-top” buildings, those where the pitch or slope of the roof is not very great. The roofing pitch used for this purpose is medium to soft, according to the climate. Most roofers prefer a pitch that can be chewed between the teeth without crumbling. In this condition it can readily be broken into small pieces without sticking to the instruments used. It is decidedly common practice for the roofers to cut back the pitch a little by putting a small quantity of tar in the kettle with it. In fact, some roofers take advantage of the fact that tar is cheaper than pitch by buying as hard a grade of pitch as they think they can use and cutting it back with coal tar to the consistence desired.

The waterproofing qualities of pitch are utilized in a similar way in tunnels, on concrete retaining walls, reservoirs, tanks, and bridges. Soft pitch is also used as a road binder and is commonly called "road tar" or "paving tar"; its properties and its use for this purpose have been discussed. In addition, it is an ingredient of bituminous paints for metal roofs and masonry work.

Pitch mixed with coal has been used in the manufacture of coke, being used in amounts up to 5 per cent of the coal carbonized. Occasionally the quality of the coke is said to be considerably improved by the addition of the pitch.

As a binder in briquetting fuel, such as coal, coke breeze, and sawdust, both coal-tar pitch and water-gas pitch are satisfactory. They are not employed much for this purpose at present in this country, although the prospects favor considerably more pitch being so used in the future. Much experimental work has been done in briquetting various fuels and the requisite properties of a suitable binder have been demonstrated.<sup>15</sup>

Numerous other uses for pitch have been developed in patent processes and otherwise that utilize its cementing or waterproofing properties, as in flume cement, roof cement for patent roofings, expansion-joint filler, binder in the manufacture of special insulating and waterproof pipe, and insulation on dry cells and batteries. It is also used in producing "pitch coke" or "tar coke," which is mentioned on page 71.

#### COMMERCIAL PRODUCTS PREPARED FROM CRUDES.

Many of the products obtained from tar by distillation are sold and used in the crude state. The crude fractions are used alone, mixed with other fractions, mixed with pitch, or as an ingredient or component part of some manufacture containing materials other than tar products. The preparation of these products does not necessarily require great skill nor very elaborate equipment. Formulas and methods of preparing a number of them are given in the following order:

1. Metal paint.
2. Roof paint:
  - a. For prepared roofs.
  - b. For shingle roofs.
3. Pole and post paint.
4. Shingle stain.

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<sup>15</sup> Wright, C. L., Briquetting tests of lignite at Pittsburgh, Pa., 1908-9, with a chapter on sulphite-pitch binder: Bull. 14, Bureau of Mines, 1911, 64 pp. Mills, J. E., Binders for coal briquettes: Bureau of Mines, 1911, 56 pp. Wright, C. L., Briquetting tests at the United States fuel-testing plant, Norfolk, Va., 1907-8: Bull. 30, Bureau of Mines, 1911, 41 pp. Wright, C. L., Fuel-briquetting investigations, July 1904, to July, 1912: Bull. 58, Bureau of Mines, 1913, 277 pp.

5. Roof cement.
6. Flume cement.
7. Disinfectants and insecticides:
  - a. Sheep dip.
  - b. Water soluble disinfectants.
  - c. Powdered disinfectants.
8. Wood preserving oils.

#### METAL PAINT.

A highly satisfactory metal paint can be prepared by dissolving pitch in the light oils obtained in the distillation of tar. Many specifications require that such a paint should dry quickly; then the lightest oil, crude naphtha, is employed as a solvent. A very hard pitch will not dissolve readily in that oil. For this and other reasons it is more satisfactory to use a medium grade of pitch. The consistence must be such that the paint will flow well under the conditions prevailing at the time it is used. However, as the light oils evaporate readily and mostly do not remain in the paint film, the more oil used per unit of pitch the thinner will be the coat or film of paint. A formula for a metal paint that will flow well and can be applied with a brush at ordinary temperatures is: Medium soft pitch, 40 gallons; crude naphtha (from tar), 60 gallons.

A convenient way of preparing this paint is to use the fresh hot pitch before it has solidified. Draw off the desired amount of pitch in a kettle and then add the oil slowly and with constant stirring. When a paint of requisite consistence is obtained, it is well to determine with a hydrometer the specific gravity at a definite temperature in order that subsequent batches can be prepared like the original. It is preferable to have some of the higher boiling oils present in such paint, but these oils are not suitable when quick drying is essential and the paint must be applied cold.

Paint prepared according to the formula given is very elastic, but this elasticity is not permanent. On surfaces exposed to atmospheric conditions and to the sun, the paint film gradually becomes brittle. The time required for brittleness to develop depends, in part, on the free-carbon content of the paint. A paint having a moderately low free-carbon content is superior to one of a high content. Finely ground opaque pigments are sometimes used in bituminous coatings with the intention of excluding the actinic rays of light which play an important part in the decomposition of such coatings. The paint withstands high temperatures fairly well and is accordingly well adapted for use on stacks and boiler fronts; it is also particularly adapted to use underground, in tunnels and on pipe.

When the paint can be conveniently applied warm or to a warm surface, light oil may be substituted for crude naphtha to good ad-

vantage. Similarly, when castings and fittings are "dipped," it is desirable to use light oil as a solvent and to employ a warm bath. Closed steam is preferable to a direct fire for heating the paint bath.

By the addition of certain resins and linseed oil, the latter in proportion varying from 15 to 25 per cent, a paint may be prepared with somewhat better weathering properties, but its cost is higher.

#### ROOF PAINT.

For shingle roofs, a black paint is made similar to the metal paint, but naphtha is not, and should not be, employed as a solvent. In fact, it is better not to distill the tar to pitch but merely until the creosote oil fraction starts to come over. The refined tar so produced may then be "cut back" with creosote oil until the consistence is such that the paint flows freely from the brush. A minimum content of free carbon assures the deepest penetration of the paint into the wood; therefore, for this purpose a tar low in free carbon is superior to one with a high content of free carbon, other things being equal. The quantity of oil and pitch or refined tar used will depend on the specific gravity of each and on the degree of fluidity desired in the paint. On the assumption that the paint is to be made from pitch and oil of the specific gravities 1.20 and 1.04, respectively, and is to have approximately 1.08 specific gravity at 60° F., the quantities required to make 100 gallons are: Pitch (1.20 specific gravity), 25 gallons; tar oil (1.04 specific gravity), 75 gallons.

If refined tar with a specific gravity of 1.16 is used with a lighter oil as solvent and thinner, the proportions may be as follows:

	Gallons.
Refined tar (specific gravity, 1.16)-----	50
Tar oil (specific gravity, 1.00)-----	50
Paint (approximate specific gravity, 1.08)-----	100

When a thinner paint is desired, proportionally more oil will be required.

A shingle roof should be thoroughly dry before it is painted, for if it is some of the paint will be drawn up into the shingles beyond the overlapping joint, a place that can not be reached with a brush. As it is along such joints that the shingles decay first, the importance of this precaution is evident. A roof coated with this paint does not retain a jet black appearance, but a slate color that usually is preferable.

In such a paint the waterproofing qualities of the bitumens are added to the strong preserving properties of the tar oils, making a very desirable combination. It is absorbed by the wood to a great extent rather than left entirely as a film on the surface, and might



with some propriety be termed a stain. Stains, mentioned later in this paper, do not include the heavier bodied tar or pitch mixtures.

Roof paint for "patent roofs"—roofs covered with specially prepared roofing paper—is not made in this way, yet does not differ much. In the discussion of metal paint (see p. 45) attention has been drawn to the fact that bituminous materials are affected deleteriously by exposure to the sun and by atmospheric conditions. The same disintegration takes place in roofing materials, which become hard and brittle simultaneously and are said to have lost their "life." The application of a bituminous paint at intervals freshens the roofing and prolongs its usefulness. As one would naturally suppose, such a paint must be heavy "bodied" and have a rather high content of bitumen.

Although it is not uncommon to find ordinary coal tar used for this purpose, the better way to prepare a satisfactory roof paint is to "cut back" a soft pitch with an oil free from naphthalene. Light oil is suitable. A lighter oil would perhaps make the paint dry quicker, but quick drying is not essential nor particularly desirable. The heavy oils make a slow-drying paint. A suitable pitch paint may be prepared by adding light oil slowly to melted pitch while the mixture is being constantly stirred. The following amounts have been used in a paint that seemed to fill the requirements: Soft to medium soft pitch, 75 gallons; light oil, 25 gallons.

The specific gravity of this paint is approximately 1.15. Mixtures of the same specific gravity do not have the same viscosity or fluidity; in other words, the fluidity of mixtures made to a specific gravity of 1.15 is not the same, regardless of the kind and quality of the pitch and oil used. Hence a paint of 1.15 specific gravity may have the desired consistence in one purpose, but it may be either too heavy, too viscous, or too thin for another. It is best to make a standard paint from the materials available and prepare subsequent batches similar to it.

A prepared paint always sells at a higher price than tar, and it is therefore not surprising that painters and roofers sometimes add rather large quantities of water-free tar to the paint.

#### POLE AND POST PAINT.

Unlike wood-preserving oil, pole and post paint is seldom purchased in large quantities; therefore, rigid specifications for it are rare. Accordingly, it sometimes happens that the small tar distillery utilizes for this purpose those tar products on hand for which there is no other market, and the paint may be sometimes straight tar, tar and naphthalene, or tar, pitch, and oil mixed.

The usual intent in painting posts and poles is to retard decay. Hence the paint may be chiefly a preservative oil of tar, a high-boiling oil that will be readily absorbed by the wood, it may be chiefly a bituminous material plus a solvent that will leave a bituminous coat on drying, or it may be a combination of both. Many mixtures can be prepared for treating poles, but it seems enough to say that a paint similar to the heavy roof paint previously mentioned or a thin mixture consisting of tar and creosote oil in approximately equal proportions can be used. The mixture must be water free and should be applied to dry timber only.

#### SHINGLE STAIN.

A stain suitable for use on new structures where it is desirable to retain the new look of the shingles is commonly composed of either "straight" creosote oil or mixtures of creosote oil and varying amounts of linseed oil. Occasionally resins also are added. On account of the difference in price, the tendency is to use considerably more creosote than linseed oil. A large percentage of light volatile oil, or an oil containing appreciable amounts of naphthalene, should not be used. Stains are often ruined by the painter's desire to make them flow more easily from the brush, for which purpose he adds kerosene. The writer has tested a number of stains now on the market that are composed chiefly of light mineral oil and creosote with drier and linseed oil. While the mineral oil may help to prevent solidifying of the pigment at the bottom of the container, it has not the germicidal or wood-preserving properties of creosote. One large oil company interested in selling petroleum products suggests the following formula for a shingle stain:

#### *Formula for a shingle stain.*

	Gallons.
Light neutral oil, sp. gr. 0.857-----	2
Turpentine substitute, mineral naphtha-----	2
Boiled linseed oil-----	1
Coal-tar creosote, extra heavy-----	4
Good liquid drier-----	$\frac{1}{2}$
Total -----	9 $\frac{1}{2}$
Color pigment, ground in oil, 1 to 2 pounds per gallon of stain.	

In the writer's opinion this stain would be improved by substituting for the mineral naphtha, crude coal-tar naphtha or some of the first portion of the light oil distilling from tar. The preserving effect on the shingles is usually not given as much consideration as permanency of color; hence the selection of the best stain for a particular purpose will depend on the preference of the user.

## ROOF CEMENT.

When prepared roofing is laid, some means of cementing the overlapping surfaces is required. Using melted pitch for this purpose is not considered here, for the reason that melting a small quantity of pitch and keeping it at the proper temperature are quite unhandy. It is preferable to use a cement that can be spread with a brush or trowel and will set as a firm waterproof film capable of withstanding the heat of the sun without melting. A material of this type may be prepared by "cutting back" a bituminous material, such as pitch, with a volatile solvent, benzol or light oil, for example, using as little of the solvent as possible. Roof cement is often prepared with the addition of other materials, such as sulphur or resins. Usually the cements "set" by the evaporation and absorption of the volatile constituent. The consistency desirable in the cement depends somewhat on the climatic conditions; therefore the proportions of bitumen and solvents must vary. The consistence should be such that the cement can be applied conveniently while warm and yet be heavy enough to hold the roofing surfaces in intimate contact. Roof cements are also used in repairing prepared roofs and prepared shingle roofs.

## FLUME CEMENT.

In irrigation and mining districts where water flumes on trestles are common it is necessary to prevent excessive leakage of water in order to protect the foundations from being washed out. It sometimes happens that water is admitted to these flumes for definite intermittent periods between which the flumes are empty. Such conditions are ideal for warping and buckling the flume timbers and resultant leakage. A common remedy is the application of a protective coating to the inside of the flume. This coating should withstand atmospheric changes as well as the action of water.

One method of reducing leakage involves mopping or brushing molten pitch, or pitch preparations, on the inside walls and bottom of the flume, when it is dry. A so-called cement successfully used for this purpose consists of a medium soft pitch (coal-tar pitch) to which has been added, while it is liquid and hot, one-half to one per cent of sulphur. The sulphur, in powdered form, is added slowly while the mixture is continually stirred to keep it from boiling over.

Because of the need of conserving water, many flumes that are partly submerged in the ground have to be waterproofed. Similar coatings of pitch or pitch preparations are used for this purpose and the surfaces coated are usually "sanded" before the coating has set.

## DISINFECTANTS AND INSECTICIDES.

Numerous antiseptics, insecticides, and disinfectants in common use are prepared with crude coal-tar products as their chief active ingredient. These preparations are used for widely different purposes, and include sheep dips, dog washes, cattle-car sprays, disinfectants for prisons, jails, hospitals, and household purposes, and disinfecting or antiseptic sprays for stables, barns, chicken houses, and street cars. In the manufacture of these preparations, consideration is given to the fact that the acid fractions, the middle-oil and creosote-oil fractions, have higher value as germicides than the other crude distillates from tar. The "straight" oil is ordinarily too concentrated to use alone, hence for this and other reasons many of these manufactured products are made in such a way that they are miscible with water in almost all proportions. Some form a clear solution and others a milky emulsion when diluted with water. The advantage of this form of preparation is that disinfectants or germicides of the different strengths required for different purposes may be prepared by merely diluting properly with water.

The preparation of these concentrated products usually involves the addition, in as small quantities as possible, of an emulsifying agent to the crude tar distillates having the highest germicidal value. In many of the ordinary disinfectants the fraction used is the oil, freed from naphthalene by chilling, that includes the crude carbolic-oil fraction and the creosote-oil fraction. Animal dips are made from the heavier fraction only, as the more poisonous carbolic acid is undesirable in such preparations. For hospital use, a product of higher grade frequently employed, is made from the refined creosote oil or from "cresols" obtained from creosote oil. The ordinary product is made by mixing a rosin-soda soap with the tar oil in the following proportions:

*Formula for a representative disinfectant.*

	Pounds.
Rosin, common grade, yellow-----	95½
Caustic soda, commercial, 98 per cent-----	14½
Water (approximately 6 gallons)-----	49
Acid tar oil, 1.025 sp. gr. (approximately 33 gallons)-----	283
Total finished product (50 gallons)-----	442

## METHODS OF MAKING DISINFECTANTS AND GERMICIDES.

Two different methods have been recommended for making these preparations. One consists of dissolving or melting the rosin in the hot oil and slowly adding, with constant stirring, the caustic soda previously dissolved in water. The other method consists in preparing a rosin-soda soap by warming the rosin with the caustic soda

solution and finally adding the oil slowly and with constant stirring. It has been the author's experience in making these preparations that the latter method is preferable, as any excess water that may have to be added can be evaporated before adding the oil, thus eliminating the loss otherwise occasioned by evaporation and lessens the danger of boiling over. To prepare the product according to the formula given proceed as follows:

Melt the rosin in an iron kettle with closed steam, using a steam coil or a jacketed kettle, and meanwhile dissolve about half of the caustic soda in about three-fourths of the water. Add this solution slowly to the melted rosin, heating and stirring meanwhile. Dissolve the balance of the soda in the remaining water and add this in the same manner. The soapy mass looks milky at first, but the rosin soap that forms will have a smooth, dark, "livery" appearance. Heating hastens the reaction and evaporates the excess water, leaving the soap in proper condition for use. If the soda and rosin do not combine readily it may be necessary to add more water, boil, and then evaporate the extra water. To the hot boiling soap add the oil, small quantities at a time, stirring continually meanwhile. After about a third of the oil is added, turn off the steam, add the remaining oil and mix well. The finished product should be clear; in thin films, as those produced on the walls of a glass vessel when agitated, it should be amber red but transparent. Cloudiness usually indicates an excessive amount of water, which can be corrected by evaporation. When a small amount of the mixture is poured into water, a white milky emulsion should result without the deposit of oil at the bottom. The water content of the finished product is usually a little less than 10 per cent. In compliance with the insecticide act of 1910, it is necessary when making interstate shipments to state the percentage of inert ingredients (water in this case) as not exceeding a definite amount. The oils used should be freed from naphthalene, for the latter causes the oil to "fall heavy" and collect at the bottom of the vessel when mixed with water; it also causes "greasiness" when present in appreciable quantities.

#### DIPS AND WASHES.

When these preparations are made especially for animal dips or washes, the creosote fraction or a derivative therefrom is employed in place of the oil used in the above formula. The same method of preparation and similar proportions as above are used. The oil used generally contains 20 to 25 per cent of phenols other than carbolic acid. For further details on dips and directions for their dilution see bulletin 107 of the Bureau of Animal Industry.<sup>16</sup>

<sup>16</sup> Chapin, Robert, Analysis of coal-tar creosote and cresylic acid sheep dips: U. S. Bureau of Animal Industry Bull. 107, 1908, 35 pp.

Washes of higher grade, for hospital use, are made in a slightly different manner. The rosin-soda soap is usually replaced by a vegetable-oil potash soap, and in place of the crude tar oils a refined product is used, which is a mixture of tar acids obtained from creosote, known as cresols. Glycerin is sometimes added. A well known, highly advertised product of this nature is composed of the following ingredients:

*Composition of a wash for hospital use.*

	Per cent.
Cresols.....	50
Potash soap.....	20
Water with a little glycerin.....	30
Total.....	100

The oils commonly used for making the potash soap are linseed oil, cottonseed oil, corn oil, or soy-bean oil, or mixtures of any of them. Linseed oil, however, saponifies more readily than the others and is more frequently used. To prepare such a solution proceed as follows:

Make a solution of caustic potash by dissolving 23 pounds of 98 per cent caustic in enough water to make 90 pounds, giving a solution with a gravity of approximately 24° B. Heat 100 pounds of raw linseed oil in a steam-jacketed kettle and when the oil is hot add the caustic a little at a time, continuing the application of heat. After about one-third or one-half of the caustic solution has been added, it may be necessary to add some cold water. Approximately 110 pounds of cold water will be required in all, but the caustic should all be added before more than one-half of the water is used. Instantaneous saponification or sudden heating and boiling over can be prevented by adding cold water when this tendency is observed. The yellow emulsion that first forms gradually changes to a clear, transparent amber-colored soft soap, which in mass looks dark. When saponification is complete and a sample of the product dissolves in water without oily particles rising to the surface, the oil or cresols may be added. The formula for the completed product thus prepared may be as follows:

*Formula for a wash for hospital use.*

	Pounds.
Raw linseed oil.....	100
24° B. caustic potash solution.....	90
Water.....	110
Cresols or acid-tar oils.....	250 to 300
Total.....	550 to 600

Considerable leeway exists for changing the relative proportions of soap and acids and for adding other substances.

The official U. S. P. product has the following formula:

<i>Official formula for wash for hospital use.</i>		Pounds.
Cresol	-----	50
Linseed oil	-----	30
Caustic potash (U. S. P.)	-----	8
Alcohol	-----	3
Water to make	-----	100

and is prepared as set forth below:

Heat the linseed oil to 70° C. (158° F.). Dissolve the caustic potash in 5 pounds of water and heat to 70° C. Add this solution to the oil and mix thoroughly; then incorporate the alcohol and continue to heat without stirring until a small portion is found to be soluble in boiling water without the separation of oily drops. While the solution is still warm, add the cresol and mix thoroughly, maintaining the temperature at 70° C. Last, add water to make the total quantity weigh 100 pounds. Note that in this process the 8 pounds of caustic potash may be replaced by 5.4 pounds of caustic soda. In making calculations, it should be remembered that U. S. P. caustic potash is approximately 85 per cent pure caustic potash and that U. S. P. caustic soda is approximately 90 per cent pure caustic soda.

Preparations like the foregoing are often rated according to their ability, in dilute solution, to destroy certain germs or bacteria. Phenol is used as the standard, and preparations that are 1 to 10 times as strong as phenol are said to have a phenol coefficient of 1 to 10.

Other acids in tar distillates have higher phenol coefficients than cresol, although they are present in much smaller proportions. Different tars contain them in different proportions. Xylenol (dimethyl-phenol) is such an acid and is said to have a phenol coefficient of 10 to 12.

Many other preparations on the market have coal-tar products as an active ingredient. Naphthalene dissolved in benzine and turpentine or other solvent is used as a spray for protection from moths, and is also a common bedbug exterminator or repellant. Drip solutions and lavatory disinfectants are other minor preparations that are so prepared. Many powdered antiseptics and disinfectants are also prepared from tar products. Flake naphthalene is used for this purpose and may be mixed with varying amounts of other powdered materials which may be inert or active. Powdered slacked lime that has absorbed a considerable amount of tar oils or of crude carbolic acid finds use as an insecticide and fungicide.

#### WOOD-PRESERVING OILS.

In addition to the pure distillates of coal tar, wood-preserving oils for some purposes are made by mixing coal tar with the heavy

coal-tar distillates. The content of tar permissible in the mixture depends upon the specifications of purchase. Not uncommonly a preservative is required with a specific gravity of 1.06 to 1.12, a free-carbon limit of 2 per cent, and a residue, on distillation in a retort to 355° C., of not more than 40 per cent. It is evident that the maximum amount of tar that can be added here depends entirely on the specific gravity, the carbon content, and distillation residues of both the oil and the tar, as is clearly shown in the example below :

*Example of a tar and oil mixture.*

	Assumed properties.		Mixture <sup>a</sup> of 1 part tar and 3 parts oil.
	Coal tar.	Tar oil.	
Specific gravity.....	1.18	1.04	1.075
Free carbon.....per cent..	6	.0	1.5
Residue over 355° C.....do...	70	10	<sup>b</sup> 25 to 30

<sup>a</sup> Parts by volume.

<sup>b</sup> Approximately.

This mixture fills the requirements of the specification, whereas neither the tar nor the creosote oil alone would pass.

As tars of low specific gravity usually contain the least free carbon, it follows that they can be used in greater proportions in tar-creosote mixtures to meet specifications such as those mentioned. It will be noted that a tar containing 20 per cent free carbon can not be used in proportions larger than 10 per cent of the total mixture and pass the specification cited above.

The use of tar in wood-preserving oils is in one sense an adulteration, but gives the oil certain desirable properties.

The presence of the bitumen of tar increases the waterproofing qualities as well as the proportion of high boiling constituents. The latter retard evaporation of the preserving oil, do not evaporate, and are desirable for other minor reasons in wood preservers for some purposes. Incidentally, this use of tar increases the possible output of wood preserver from a plant and the total available supply; also it decreases the average cost per gallon. To make possible the utilization of the maximum percentage of tar in these mixtures, the tar is sometimes filtered and centrifuged to reduce the percentage of free carbon as much as possible.

#### PRODUCTS OBTAINED BY FURTHER REFINING THE CRUDE DISTILLATES.

Highly refined coal-tar and chemical products are not prepared in the tar distillery, but are usually manufactured in a separate plant from the cruder materials supplied by the tar works. How-



ever, some of the larger distilling plants prepare crude and refined benzols, cresols, and naphthalene. War conditions brought about changes in the operation of tar works, some crude chemical products being made by plants that under ordinary conditions had no inducement to consider manufacture. Products whose manufacture is briefly considered here are as follows: Crude and refined benzol, solvent naphtha, crude and refined toluol, xylol, crude and refined carbolic acid and cresol, crude and refined naphthalene, and crude and refined anthracene.

## BENZOL AND SOLVENT NAPHTHA.

Crude naphtha, the first distillation fraction from tar, contains benzol, toluol, and other hydrocarbon oils. The initial step in refining naphtha is washing with dilute (12 per cent) sulphuric acid by agitation. Then the naphtha is allowed to settle, separated from the acid, washed with water, and finally washed with dilute (about 6 per cent) caustic-soda solution. These washings remove a small percentage of the original volume and include substances known as "bases" and "phenols." The purified oil is redistilled with closed steam in special stills. In some stills live steam is also used. The method of distillation or fractionation employed depends on the product desired, whether 90 per cent benzol, 50 per cent benzol, or another similar product. The fact that the various constituents of crude naphtha have different boiling points is utilized in separating by distillation. Table 8 showing 90 per cent benzol signifies that product from naphtha which on distillation will yield 90 per cent distillate at 100° C. Accordingly, 50 per cent benzol may contain a considerably larger proportion of higher boiling oils, such as toluene and xylene. Sometimes, particularly when an especially pure or high-grade benzol is desired, a double distillation is made.

TABLE 8.—*Some properties of the light oils from coal tar.*<sup>a</sup>

Oil.	Color.	Distillation.	Specific gravity at 60° F.	Wash test, not darker than—	Flash point (A. S. T. M. closed tester method).
Pure benzol b...	Water white.	100 per cent within 2° C.....	0.875 to 0.885	No. 4.	Below freezing.
100 per cent benzol.	.....do.....	100 per cent at approximately and not above 100° C.	.875 to .885	No. 6.	Do.
90 per cent benzol.	.....do.....	Approximately and at least 90 per cent at 100° C.	.870 to .882	No. 6..	Do.
50 per cent benzol.	}.....do.....	{Approximately and at least 50 per cent at 100° C.	}.868 to .880	No. 6..	About 23° F.
		{Approximately and at least 90 per cent at 120° C.			
		{Between 79.5 and 135° C.....			
Motor benzol...	.....do.....	{Approximately 85 per cent at 100° C.	.870 to .882	No. 6..	.....

<sup>a</sup> As published by The Barrett Co. in its pamphlet "Refined coal-tar products."

<sup>b</sup> Pure benzol should crystallize at approximately 5° C.

TABLE 8.—*Some properties of the light oils from coal tar*—Continued.

Oil.	Color.	Distillation.	Specific gravity at 60° F.	Wash test, not darker than—	Flash point (A. S. T. M. closed tester method).
Straw-color benzol.	Straw.....	At least 80 per cent at 100° C.....	.862 to .882	None.	.....
Pure toluol.....	Water white.	100 per cent within 2° C.....	.864 to .874	No. 4..	+7° F.
Commercial toluol.	{...do.....	{Not over 5 per cent at 100° C.....	{.864 to .874	{No. 6..	{About +15° F.
		{Approximately and at least 90 per cent at 120° C.....			
Straw-color toluol.	Straw.....	At least 80 per cent at 120° C.....	.862 to .872	None.	About +17° F.
Pure xylol.....	Water white.	100 per cent between 137 and 142° C.	.860 to .870	No. 6..	About 82°
Solvent naphtha.	{...do.....	{Not over 5 per cent at 130° C.....	{.862 to .872	{No. 14 <sup>c</sup>	{About 80° F.
		{Approximately and at least 90 per cent at 160° C.			
Crude solvent naphtha.	Dark straw ..	At least 80 per cent at 160° C.....	.862 to .882	None.	Do.
Hi-flash naphtha.	Water white.	100 per cent between 150 and 200° C.	.870 to .880	No. 9 <sup>d</sup> .	Not below 100° F.
Crude heavy solvent naphtha.	{Amber to red.	{Not over 10 per cent at 160° C.....	{.940 to .986	{None.	{Not below 90° F.
		{At least 90 per cent at 200° C.....			
Heavy naphtha.	{Deep amber to dark red.	{Not over 10 per cent at 160° C.....	{.925 to .950	{None.	{About 115° F.
		{About 70 per cent at 200° C.....			

<sup>c</sup> 66 acid 5 minutes.<sup>d</sup> 60 acid 5 minutes.

One method of working up the washed crude naphtha is by distilling it with closed steam, thereby separating two fractions—crude benzol and crude solvent naphtha—and a heavy residue. Open steam is sometimes used during the latter part of the distillation. The crude benzol is collected until a sample of the distillate from the condenser, on distillation in a laboratory retort, shows the first drop at 110° C. The second fraction—"crude solvent"—is now collected until the oil coming from the condenser has a specific gravity of approximately 0.968 at 60° F. The residue is worked up with heavier distillates. The crude benzol is then washed with one-half to 1 per cent of its volume of concentrated sulphuric acid and subsequently with water, with dilute caustic soda solution, and finally with water again. This washed product is rectified and the products collected are 90 per cent benzol and 50 to 90 per cent benzols. By a second rectification of the 90 per cent benzol, a pure product—pure benzol—is obtained.

The crude solvent naphtha is washed similarly with acid, water, and alkali and is rectified into a fraction known as 90 per cent at 160° C. However, various solvent naphthas are prepared according to their intended uses. Moreover, by further rectification solvent naphtha yields a number of products as, for example, toluol and xylol. The residue from the last benzol rectification is added to the crude solvent naphtha and the residue from the further distillation of this fraction is utilized with higher boiling fractions.

Chemically pure benzol, known also as benzene, is a definite chemical compound, and is quite different from the petroleum prod-

uct known as benzine. It boils at 80° C. and “freezes”—solidifies to a mass of crystals—at approximately 5° C. Its specific gravity is 0.885 at 60° F. This product is of great importance commercially, as it is the source from which aniline and many dyes, as well as other chemical products, are made. Synthetic carbolic acid is also prepared from benzol. Pure benzol is not used as a motor fuel, although mixtures containing it with toluol, solvent naphtha, and gasoline are particularly suitable for this purpose. A large gas company producing quantities of this oil recommends as motor fuel a mixture containing:

*Recommended composition of a motor fuel.*

	Per cent by volume.
Toluol.....	50
Benzol.....	40
Solvent naphtha.....	10
Total .....	100

The benzol, toluol, and solvent naphtha are obtained from city gas by absorption—stripping—and not from coal tar.

Benzol and gasoline mixtures containing 50 to 70 per cent of benzol make satisfactory motor fuel. Toluol may also be used successfully if added to such a mixture. On starting a motor in cold weather, less difficulty is experienced from these mixtures than from the formula recommended above.

More energy is stored in such a motor fuel than in an equal volume of ordinary gasoline, the relative values being approximately as follows:

*Heating value of gasoline and benzol.*

	Heat of combustion per pound of combustible, B. t. u.	Heat of combustion per gallon of combustible, B. t. u.
Gasoline.....	20,000	122,800
Pure benzol.....	18,054	133,100

It is claimed that use of such a fuel in an automobile will give 25 per cent more mileage.

Benzol is preeminently a solvent; it dissolves soap and many other substances containing water. It is invaluable in the manufacture of paint, for its use in small quantities in mixed paints prevents “livering” or saponification due to alkaline tendencies of the paint. It is used in paint for priming and is said to give a firmer bond between the paint film and the wood. The varnish and the rubber industry also make extensive use of the solvent properties of benzol.

The uses of benzol and of products obtained from it can be shown as follows:

*Use of benzol.*

Benzol.....	Aniline.....	Dyes of various colors. (Explosives. Drugs. Antiseptics. Dyes.
	Synthetic carbolic acid.....	Motor fuel.
	.....	Solvents, in paint, oil and rubber industry.
	.....	Cleaning solutions.
	Miscellaneous chemical products...	Flavoring and perfume materials.

Solvent naphtha is used as a solvent much the same as the benzols. Because of differing in flash point and boiling point solvent naphtha is preferable to benzol for many of the uses to which the latter is put. It is also used in the refining of anthracene and in other chemical washing processes.

TOLUOL.

Pure toluol (also known as toluene) is a colorless oily liquid with an odor somewhat like that of benzol. Its freezing temperature is low, nearly  $-100^{\circ}$  C. Its boiling point is  $111^{\circ}$  C. and its specific gravity is 0.872 at  $60^{\circ}$  F. Its chemical properties are in many respects like those of benzol.

Commercial toluol, a product of which 90 per cent will distill below  $120^{\circ}$  C., is usually obtained from crude benzol. The crude benzol distilled between approximately  $100^{\circ}$  and  $120^{\circ}$  C. is termed commercial toluol and has a specific gravity of 0.862 to 0.870 at  $60^{\circ}$  F. The uses of this product are similar to those of the benzols. Having a higher boiling point it is less volatile and dries more slowly when used in varnishes and similar preparations—an advantage in many of these preparations. It is a valuable ingredient in turpentine substitutes.

Commercially pure toluol may be prepared from the 90 per cent toluol by further distillation and rectification. As the boiling point of pure toluene is  $111^{\circ}$  C., the fraction separated begins to boil at  $111^{\circ}$  C. and to yield 95 per cent at about  $111.8^{\circ}$  C. or 100 per cent within  $2^{\circ}$  of the boiling point of toluene, that is,  $111^{\circ}$  C.

Chemical plants work this product into a more refined product. Commercial toluol is the source of the explosive T.N.T. (trinitrotoluene), of dyes for cotton, of synthetic flavoring, and perfume materials, and of other chemical compounds.

XYLOL.

Xylol is another commercial product from the light fraction of coal tar. It has a higher boiling point than benzol or toluol and is

recovered from the distillate residues from the preparation of pure benzol and pure toluol. Pure xylene exists in a number of slightly different forms having boiling points ranging from  $137.5^{\circ}$  to  $142.6^{\circ}$  C. Its refining is like that of benzol and toluol. A fraction is collected a large percentage of which will distill within close temperature limits, approximately  $136^{\circ}$  and  $140.5^{\circ}$  C., the limits varying according to the specifications of purchase. The crude product is a water-white to pale yellow oil with a specific gravity of 0.865 to 0.87+; the specific gravity of purified xylol is 0.87.

Xylol is a satisfactory solvent and, as its high boiling point indicates, does not volatilize rapidly in the air at atmospheric temperatures. Therefore, it is used for purposes requiring the use of products that volatilize slowly. Pure xylol is the source of a number of synthetic chemical compounds.

Weiss estimated that in 1911 the coal-tar solvents used in the United States were apportioned as follows:

*Uses of coal-tar solvents in 1911.*

	Per cent.
Paint and varnish industry.....	47
Rubber and rubber cement.....	18
Imitation-leather industry.....	10
Chemical manufacturers .....	11
Miscellaneous .....	14
Total (2,000,000 gallons).....	100

These figures do not represent the present distribution of coal-tar solvents. The World War with the development of the gas-stripping process and recovery of toluol and benzol, the increased use of explosives, the development of the chemical industries, and the use of benzol and toluol in motor fuels have altered conditions which are not stable at the present time.

CARBOLIC ACID.

The middle-oil fraction obtained by distilling tar is the oil "worked" for carbollic acid. Acid portions obtained in refining the lighter fractions are combined with this fraction and refined. Pure acid usually is not prepared at the tar works, but at a special chemical plant, and smaller tar works do not even undertake to produce crude carbollic acid. In some parts of the country the writer has found crude carbollic oil being sold under the name "crude carbollic acid." The crude oil as it comes from the still contains about 20 to 40 per cent naphthalene and 15 to 35 per cent of tar acids, which include cresols and carbollic acid. There is 5 to 12 per cent of carbollic acid in this oil. The percentage of tar acids in tars is shown in Table 2, page 9.

The method of "working up" the acid distillates from tar depends on the character of products sought, which may be a single product like crude acid containing phenol and cresols, or a number of products such as crystallized carboic acid, crude carboic acid, and refined cresol. The general process of manufacture is much the same, but the washing methods, strengths of washing solutions, and distillation fractions separated are of course dissimilar. Details of the process can not be described here, but only the basic principles of refining considered.

The separation of two or more allied substances depends on differences in their properties. Phenol and cresols have much the same chemical properties, and their separation from the nonacid bodies is based on their solubility in dilute caustic soda solution, which yields concentrated acid when the soda is neutralized with sulphuric acid or its equivalent. They actually combine chemically with the soda solution forming carbolates and cresolates. The separation of the tar acids is based on a difference in boiling point. Pure phenol boils at  $182.6^{\circ}$  C., but cresol has a much higher boiling point,  $192^{\circ}$  to  $202^{\circ}$  C. Cresol exists in three modified forms known as three distinct cresols, with boiling points  $192^{\circ}$  to  $202^{\circ}$  C. As used here, the word "cresol" means a mixture of the three in any proportions.

When only a crude acid, one that contains the cresols and phenol, is desired, the middle oil and the acids recovered from the light oil or with the last portion of the light oil distilled are given fewer washings and distillations than in preparing the purer product, and stronger caustic-soda solution is used.

When pure refined phenol is sought the first washings are made with weaker soda solutions and the subsequent washings with stronger solutions. The weaker solutions yield the highest grade of phenol.

Crude cresylic acids are prepared from the residue acid in the separation of phenol. Pure cresol is prepared from the crude product by distillation and fractionation. Commercially the name "carboic acid" is not applied to phenol alone; it is sometimes given to crude tar acids containing cresols mixed with high or low percentages of phenol. Crude carboic acid was recognized in the United States Pharmacopœia, 1890 edition, as consisting of 90 per cent tar acids.

Briefly, middle oil may be refined as follows: Chill the oil and drain the liquid portion from the naphthalene. Redistill in a similar manner as tar is distilled, using a still with a dephlegmating head.

The fraction collected between  $165^{\circ}$  and  $200^{\circ}$  C. is termed "carboic-acid oil" and is treated further for the acid. It has a specific gravity of 1.0 to 1.005 and contains considerable naphthalene. The fractions obtained may be, approximately:

*Fractions from middle oil.*

	Per cent.
Up to 150° or 165° C., when no more water comes over (used as crude benzol)-----	1 to 4
165° to 200° C. (carbolic-acid oil)-----	18 to 22
200° to 220° C. (naphthalene oil)-----	25 to 45
Residue (and loss 1 to 2 per cent)-----	56 to 29

The naphthalene oil is chilled and centrifuged; containing 25 to 30 per cent of tar acids (mostly cresols) and is sold as "crude commercial carbolic acid." The residue may be used in preserving oils, creosote and similar crude products. The carbolic-acid oil fraction collected between 165° and 200° C. is separated from naphthalene, then washed or agitated with a warm solution of caustic soda, which unites with the acid to form a water-soluble compound. After it settles this compound of carbolic acid and soda—sodium phenolate—is separated from the remaining oil, treated in the same manner as before with the proper amount of sulphuric acid, and evaporated to the proper concentration. The tar acids liberated are separated after settling as "crude carbolic acid," which is distilled. The fractions collected are as follows:

*Fractions from crude carbolic acid.*

Up to 180° C.-----	Chiefly water.
180° to 200° or 205° C.-----	Main carbolic acid fraction.
205° to 220° C.-----	Chiefly cresols.

The range of crystallization of carbolic acid is from the 180° to the 205° C. fraction. The carbolic acid is not absolute phenol yet, being contaminated with some cresol. Further fractionation of the crystallizable portion—closer to 182.6°, the boiling point of phenol—yields pure carbolic acid. The mother liquor draining from the crystallized acid in the crystallization tanks is chiefly cresol and is used in making various disinfectants and antiseptic washes and in preparing pure cresol.

Pure phenol (U. S. P.) contains not less than 97 per cent phenol; it occurs in colorless needle-shaped crystals or as a white, occasionally reddish, crystalline mass; it has a characteristic, somewhat aromatic odor. An aqueous solution (1 to 15) is clear. Phenol melts when gently heated, the congealing point being not below 38° C. and liquifies on the addition of about 8 per cent water. Ten grams heated on a water bath volatilizes without leaving more than 0.05 gram residue. The vapors are inflammable.

The alkaline—caustic soda—washings of the lighter tar distillates contain, when refined, considerable proportions of tar acids; these are usually added to the crude product from the middle oil and refined. The presence of these acids, particularly in light oil, is to be expected when the latter fraction is collected between 170° and 210° C.

A commercial crude cresylic acid is prepared during the manufacture of refined carbolic acid or phenol. The fractions, which have a higher boiling point than desired in the phenol fraction, obtained from redistillation in the recovery of phenol, are rich in cresols and are further refined for a purer product. Different qualities of mixed cresols are on the market and almost any grade can be purchased on specification. Some of the commonly marketed products are: Cresylic acid, 50 per cent; cresylic acid, 95 to 97 per cent, dark; cresylic acid, 97 to 99 per cent, straw color; and cresol, U. S. P.

Cresylic acid is a name commonly applied to the different tar acids, chiefly or entirely cresols, that boil above  $185^{\circ}$  C. The lower grades, however, often contain appreciable amounts of phenol. The United States Pharmacopœia defines "cresol" as a mixture of isomeric cresols obtained from coal tar. Its specific gravity is 1.03 to 1.038 at  $25^{\circ}$  C. Not less than 90 per cent by volume distills between  $195^{\circ}$  and  $205^{\circ}$  C. It is a colorless or yellowish to brown yellow, highly refractive liquid, becoming darker or assuming a reddish tint with age and on exposure to light, and having a phenol-like, sometimes empyreumatic, odor.

In preparing cresol the acid is air blown in order to remove some of the sulphur compounds and other impurities that impart a disagreeable odor.

The various tar acids described are used in the preparation of numerous germicides and antiseptics, in the manufacture of other chemical products, in soaps and soap preparations, and in numerous other specialties.

#### NAPHTHALENE.

The solids crystallizing from the crude distillates of coal tar and from some of the distillates obtained during the rectification of benzol, naphtha, and tar acids are chiefly naphthalene and naphthalene compounds. These solids are freed from oil as far as possible by settling, chilling, and draining. The solids remaining are pressed in a hydraulic or similar press to extract the oil which they still retain. The name "crude naphthalene" is applied to the solid material that has been separated from oil by chilling and draining and sometimes is applied to the product from the press.

A purer product is obtained by hot pressing, which consists in pressing molded cakes of the crude naphthalene in a press having its plates heated, usually with steam. The naphthalene obtained is fairly satisfactory but is not absolutely pure. It is not snow white but pinkish, in which form it has many uses. Pure naphthalene is obtained by refining.

Commercially pure solid naphthalene is prepared as follows: The cakes from the hot press are broken up and washed with a hot



caustic-soda solution in a closed tank or kettle provided with an agitator and a steam connection for heating. The naphthalene is here fused and freed from the tar acids which combine with the caustic soda. The wash solution is drained off and the residue in the kettle is given a hot wash, which is followed by a washing of strong sulphuric acid, several washings with water, and a wash with a weak solution of caustic soda, which is followed by a water wash. This washed hot naphthalene, now liquid, is distilled in the same way as middle oil. The fraction coming over above  $210^{\circ}\text{C}$ .—usually up to  $225^{\circ}$  or  $230^{\circ}\text{C}$ .—may be molded directly as solid naphthalene.

Flake naphthalene is prepared by subliming the cake from the hot press or sometimes that from the cold press. In addition, the product obtained by centrifuging the solids from the crude distillates is sometimes used. A fine grade is obtained by subliming the wash product from the hot press as prepared for distillation.

Sublimation is a simple process, the naphthalene being heated in shallow pans by a steam coil or other suitable means and the vapors being condensed in a large special chamber or room (see fig. 10). The naphthalene thus condensed forms a deposit on the walls, ceiling, and floor of fluffy white flakes, which have a characteristic penetrating odor and are insoluble in water. Naphthalene is soluble in ether, alcohol, benzene, toluene, and the essential oils.

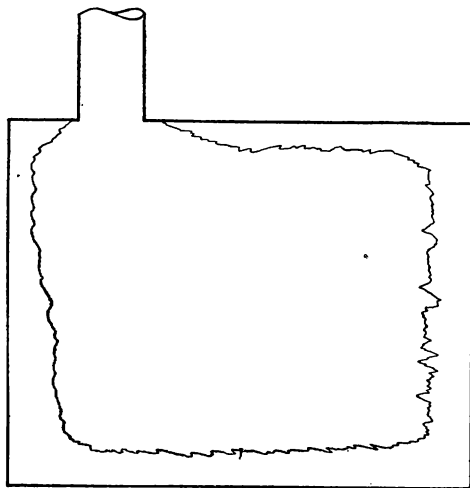


FIGURE 10.—Naphthalene chamber, showing flake naphtha condensed on walls, ceiling, and floor.

#### ANTHRACENE.

Anthracene is not usually produced in small tar works except as it exists in the anthracene-oil fraction obtained in distilling tar. In such plants it is common practice to include this fraction with the creosote fraction, thereby enhancing the value of the latter as a wood preservative.

The crude product is obtained by cooling the anthracene-oil fraction and allowing the solids to separate and the oil to drain off. After the oil is drained from the solids, the latter are bagged and pressed or "whizzed" (centrifuged) to expel the oil still retained with the solids. This crude anthracene is usually sold as such. It

amounts to about 5 or 10 per cent of the total distillate fraction from which it was obtained and contains approximately 15 to 35 per cent of anthracene. Different tars yield different amounts of anthracene. To purify the crude product further, it is either ground and agitated with hot solvent naphtha and drained, or is washed in a whizzing process with solvent naphtha. The dried product made in either way contains approximately 70 to 80 per cent of anthracene.

A high-grade commercial anthracene is sometimes prepared by re-distilling the crude anthracene oil obtained in the distillation of tar and separating a fraction that includes the distillate with a specific gravity higher than 1.07 at 60° F., the change or "cut" being made when the distillate coming over has a specific gravity of approximately 1.25 to 1.30 at 60° F. This fraction is cooled, drained of oil, pressed and washed, and sometimes sublimed. The sublimation process is like that employed for purifying naphthalene except that the inclosed anthracene pans are heated by direct fire and superheated steam is blown directly on the melted anthracene and a water spray is used to condense the product. The commercial grade of anthracene is known as 80 per cent anthracene. Its further treatment is left to the alizarin works or other chemical plants.

### SPECIFICATIONS.

The necessity for the various, and, in many cases, widely different specifications for certain tar products is evident from the many varieties of tar, all giving more or less similar products on distillation, and from the many ways in which these tars are distilled, fractionated, refined, and mixed. When a complex product of tar is required and its most desirable and least desirable components are known, it is natural for the consumer to include in his specification the maximum amount of the desirable ingredient that the manufacturer can produce and to exclude excessive amounts of the undesirable. These limiting figures have been a benefit to the tar industry rather than a hindrance, since they have developed research into further uses and have increased our knowledge of the properties of these products.

Specifications are drawn up for definite purposes and have definite meanings, some of which are not always evident to the casual reader. For example, a particular timber preservative may be defined as containing a definite minimum amount of matter insoluble in solvents such as hot benzol. This is in fact a way of limiting the proportion of free carbon that will be tolerated in the required product, free carbon being the only likely ingredient insoluble in hot benzol, and shows the tar distiller at once how much tar, if any, can be added to pure creosote oil and still have the product comply with the specifications. The full meaning of a specification can be appreciated and

understood only by knowledge of the properties and uses of the various products and their ingredients.

Although specifications, with their frequent revisions, are becoming more definite and restrictive, thus limiting the use of the individual ingredients, the efforts of the tar distiller to produce the maximum possible amount of some products tend to neutralize the ill effects of restrictions. An example is the increased percentage of coal tar permissible in some wood-preserving oils as the distiller has used filtering or centrifuging to remove the objectionable free carbon. When the only limiting factor regulating the addition of tar is that the oil must contain, for example, not more than 2 per cent of free carbon, it is evident that such oil could not contain more than 10 per cent of a tar containing 20 per cent of free carbon. If the tar is filtered while hot and its free carbon content reduced to 6 per cent, not more than 33 per cent of it can be used.

The manufacturer of creosote desires to limit the use of coal tar, primarily because he knows the difficulty in obtaining the required penetration and saturation when much is present; and realizes that the free carbon in the tar is largely the cause. The tar distiller, in eliminating free carbon, not only makes possible the use of a larger proportion of tar but does so in a way that makes it impossible to determine from the per cent of free carbon in the finished product what percentage of tar is present. If it is desirable for other reasons to limit the percentage of tar allowable, additional regulations are imposed, such as limiting the amount, the physical properties, and maximum specific gravity of the residue remaining above defined temperatures on distillation. With other products as well, adulteration is prevented and purity obtained by specifying boiling points, specific gravity, solubility, volume of fractions at given temperatures that are obtainable on distillation, color, odor, and viscosity.

To manufacture tar products that comply with some specifications is not difficult, but occasionally a specification compels the distiller to use his utmost skill to produce the grade or quality specified.

#### SPECIFIC GRAVITY.

One of the simplest methods of designating certain crude tar distillates is by defining the specific gravity of the fraction required. Under the circumstances, it is only necessary for the still operators to separate a fraction with the specific gravity named. If it is desirable to make more than a normal output of this product it is only necessary to add to the separated fraction a quantity of the fractions with a lower and a higher specific gravity. For example, if a crude distillate having a specific gravity of 1.02 is required, the supply can



a lower boiling point than the heavier ones and the lighter constituents must be removed by distillation or otherwise until the product has the desired boiling point. Mixing some of the low-boiling fractions with varying proportions of a much higher boiling fraction yields a product with an intermediate boiling point.

The melting point commonly used in specifications for such substances as pitch and pitch products is another way of expressing the consistence of a pitch. The more oil distilled from them the harder they are and, correspondingly, the higher is the melting point. When the melting point is too high to pass the specifications, it is common practice to add enough liquid, or lower boiling, fractions to lower the melting point to the desired limit. Naphthalene, creosote oil, anthracene oil, or residue oils from the refining stills may be used. Anthracene oil or creosote oil is preferable, and naphthalene is not to be recommended.

Specifications for some of the refined products from tar also have a clause covering the melting point.

As every pure chemical product has a definite melting point, the purity of commercial products can, to a certain degree, be estimated from such tests. The failure of a finished product to comply with melting-point requirements usually means that additional refining is necessary. Sometimes a specification calls for a product that when distilled to a given temperature will have a certain minimum or maximum amount of residue with definite characteristics. Thus, 90 per cent benzol has a residue of less than 10 per cent at 100° C., motor fuel must distill to dryness at about 200° C., and a wood-preserving oil must have a residue not greater than 40 per cent at 355° C., and the residue must not be brittle. To comply with such specifications it is necessary in distilling to so collect the various fractions that a preponderance of the undesirable high-boiling or low-boiling substances is not present in the finished product. For example, should the residue of the wood-preserving oil be greater than 40 per cent at 355° C., it is necessary to add enough oil that will distill below 355° C. to the product to reduce the residue to the desired amount on distillation. Brittleness of the residue usually indicates a high percentage of free carbon, which may be decreased by reducing the percentage of tar in the mixture or by using a "low carbon" tar.

#### FLASH POINT.

The "flash point," that is the lowest temperature at which the vapors arising from an oil will ignite from a small flame and go out without igniting the oil, is used in specifications to control the proportion of low-boiling combustible ingredients. The distiller who is acquainted with the flash point of the numerous distillation fractions can control this factor by making "cuts" at the proper time.

In general, the flash point is lowered as the per cent of low-boiling oils in a given mixture is increased, and vice versa. The flash-point test of a dip paint to be used warm is of value in determining whether or not the paint may be safely used indoors; the test is also of great value in specifications for motor fuel, creosote preservative, solvent oils, pitch preparations, and similar products.

When a product with a certain fluidity at a stated temperature is desired, a viscosity stipulation is inserted in the contract. In general, distillates of low specific gravity are more fluid than distillates of high specific gravity, although this is not universally true as the temperature and other factors affect fluidity.

#### MEETING SPECIFICATIONS.

When a number of limiting factors are included in a single specification, it is sometimes more difficult to make the adjustments or changes that will give the material the specified properties. A change in the proportions of the ingredients in a mixture will probably change more than one of the properties of the mixture. The writer can not give a method of manufacture that will apply to the specifications covering all tar products, but can show by example some of the considerations involved in manufacturing products to comply with specifications.

Assume that a bituminous concrete tar is required to meet the following specifications:

1. Shall not foam at-----° C-----	150
2. Specific gravity at 25° C. (77° F.)-----	1. 20 to 1. 30
3. Bitumen soluble in carbon bisulphide, not less than---per cent---	85
4. Distillation yield to 170° C-----do-----	0. 0
Distillation yield 0° to 270° C., not more than-----do-----	10
Distillation yield 0° to 315° C., not more than-----do-----	20
5. Distillate, total specific gravity at 25° C-----	1. 03
6. Distillation residue—melting point, cube method, not more than-----° C-----	75

Here the product required is evidently a soft pitch, as the residue from distilling off less than 20 per cent at 315° C. has the melting point of a hard pitch. The specific gravity of the distillate, according to item 5, is 1.03, and it comes over above 170° C., hence one may conclude that no light oils are present in appreciable amounts and that the product is, perhaps, a tar that has been distilled to about 200° C. That it is free from water is shown by its not foaming at 150° C. An average coal tar distilled to about 200° C. would have a specific gravity within the limits prescribed, although for some tars it might be below the lower limit. The maximum amount of free carbon allowed is 15 per cent, as at least 85 per cent of the product is soluble in carbon bisulphide. Accordingly, one may esti-

mate that the original tar contained 12 per cent of free carbon, for about 20 per cent of the original tar has been removed as light oils in preparing this product.

In "working up" a tar for the first time into a product of this nature, it is well first to distill a sample on a laboratory scale, often saving considerable work thereby, for after a product is prepared and is found to be lacking in some qualities, further treatment is not always easy.

In preparing this road tar, it is essential that the original tar contain less than 12 per cent free carbon or that it, or part of it, should have some of the free carbon removed. When free from water the product will not foam at 150° C. The finished product can easily be made to have a specific gravity within the limits given by "cutting back" pitch with heavy oils. No minimum limits of the yield on distillation are set, therefore there is considerable leeway for the manufacturer in adding the oils that will give the required specific gravity. Should the fractions coming over on distillation be greater than prescribed, the addition of harder pitch, which contains practically no oils distilling at the temperatures given, will remedy the defect. Under normal conditions the total distillate will have a specific gravity of 1.03, but should it be too low, the addition of high-boiling oils such as creosote will remedy this defect. When honestly prepared, a product that complies with the first five requirements will usually comply with the sixth as well. However, when an attempt is made to "cut back" a very hard pitch with a little middle oil or light oil, the distillation will probably yield a residue with a melting point above the limit of 75° C.

An additional requirement is sometimes added in specifications for such a material, namely, viscosity. In general, there is no difficulty in obtaining a product with the viscosity usually specified, for small additions of oil make the product more fluid. The oil used depends on the quantity distilling at the temperatures named, 270° and 315° C. Some manufacturers have used naphthalene to control viscosity. A small amount of naphthalene will materially alter the viscosity of a pitch of a given melting point, but the addition of naphthalene in appreciable proportions is not to be recommended.

#### REQUIREMENTS FOR SPECIAL OILS.

In specifications for creosote oil or for wood-preserving oils a number of requirements are included, all of which help the manufacturer to understand what fraction or fractions are wanted. The stated requirements for specific gravity and distillation range show how the distillates from tar must be separated at the still. The maximum amount of light oils that is allowable can also be estimated roughly. The free carbon and the residue requirements

show clearly how much tar may be added; the specific gravity also limits the proportion of tar. The percentage of tar acids required and allowed designates whether or not an oil that has had the acids removed can be used and whether crude acids can be included as a considerable part of the oil. The acids normally present in the high-boiling distillates are usually desirable in the proportions as found, but the presence of an undue amount of phenol is said to have a deleterious effect on the wood treated. The amount of naphthalene permissible is sometimes limited to prevent the wholesale "dumping" of this product, which is sometimes unsalable, into the oil, where a large proportion of it is undesirable. Adulteration with mineral oils is guarded against by specifying the minimum specific gravity of the fractions obtained on distilling a sample, by the amount of matter unsaponifiable by sulphuric acid and caustic soda, and by the odor during distillation.

One specification previously mentioned requires an oil that is a pure distillate from coal tar, with a specific gravity of 1.08 to 1.12 at 25° C. and not more than 1 per cent of matter insoluble in hot benzol and chloroform. Regardless of any other requirements, it is evident that when tar is distilled as described to produce a medium pitch a very small fraction is obtained with a specific gravity above 1.08. Apparently, either anthracene oil or a mixture of this oil with the last creosote coming over during the distillation of tar is desired; to produce a small amount of this, a large amount of tar must be distilled. The endeavor to increase the production of this oil has led some manufacturers to add to creosote oil an appreciable percentage of tar containing practically no free carbon; thus the specifications are complied with fully except the requirement that "the oil shall be a pure distillate of coal tar." Strict requirement may be accomplished honestly and the production increased by distilling the tar to a very hard pitch or carbonizing it. The price obtained for the oil and for the resulting hard pitch or coke is one of the controlling factors that determine how best to prepare these oils.

Some specifications stipulate products that are practically impossible to prepare. Such specifications usually are drawn up by inexperienced men and can be altered. An example is the specification of a low-gravity oil with only high-boiling fractions and a large residue over 355° C. and vice versa. Again, the quantity of distillate obtained at different temperatures may not be compatible with other specified requirements. As a rule their incongruities are quickly recognized when the properties of the tar employed to manufacture the specified products are understood.



**CARBONIZATION OF COAL TAR—DISTILLATION TO COKE.**

When coal tar is distilled to a soft pitch, the volume of pitch produced is approximately twice that of the oil distillates. Coke-oven tars and vertical retort tars do not yield so high a percentage on distillation. As there is a greater demand for the oil than for the pitch, it is desirable to increase the percentage of oil, simultaneously reducing the quality of the pitch. In some plants this is being accomplished by making a very hard pitch which is subsequently powdered and used as fuel; the yield of oil is thus increased from 32 per cent of the tar to 50 per cent of it.

By distilling at a red heat to a solid residue, coke yield of oil is still higher, and the coke is a correspondingly smaller percentage of the original tar. In making such a distillation—that is, coking the tar—the author's results in a small 6-ton still checked very closely those in the laboratory. The following table shows the plant results obtained in each process with the same quality of retort-gas tar:

TABLE 9.—*Yield from distillation of coal tar.*

Products obtained.	Distilled to a medium soft pitch.	Distilled to a coke.
	<i>Per cent.</i>	<i>Per cent.</i>
Water.....	2	2
Total distillate.....	27	61
Pitch.....	70	0
Coke.....	0	30
Loss.....	1	a 7
Total.....	100	100

a Lunge reports a loss of more than double this amount.

It can be seen that the percentage of high-boiling substances recovered when coke is produced instead of pitch is increased decidedly. A rather large proportion of this increment is solid; it is pasty, greasy, flaky, and resinlike as it comes from the still. The color of the distillate coming over is greenish red early in the distillation, but later is yellow, orange red, and maroon. The color changes may differ somewhat when other tars are distilled.

The total distillate from distilling coal tar, not pitch, to coke is a heavy, rather viscous liquid at 25° C., and at room temperature 20° C. Tests by the author gave the following results:

*Properties of total distillate.*

Specific gravity at 25° C., 1.085.

Distillation of 100 grams in an 8-oz. retort (thermometer bulb  $\frac{1}{2}$  inch

above level of liquid) gave fractions:

Per cent by weight.

0 to 150° C.....	0.00
150 to 210° C.....	0.00
210 to 235° C. (oil).....	8.22

Distillation of 100 grams in an 8-oz. retort, etc.—Continued.		Per cent by weight.
235 to 315° C. ( $\frac{1}{2}$ solid) .....		36.43
315 to 355° C. (pasty) .....		13.95
Residue (very soft) .....		41.00
Loss .....		.40
Total .....		100.00

The light oils come over at a higher temperature than when the total distillate obtained in the production of medium pitch is distilled. The total distillate of which the analysis has just been given will comply with many specifications for timber-preserving oil without further change or addition; thus the supply of oil for timber preserving is increased greatly. When this tar is distilled to a medium pitch, only about 10 to 20 per cent of the original tar is considered suitable for timber preserving. When coke is made, however, over 60 per cent of the original tar may be so used, or rather will "pass the specifications." This differentiation is made because the light oils that are apparently not present by analysis are actually a part of this oil but distill at higher temperatures.

The coke from this process is open, porous, firm, and hard, either silver gray or shiny black when thoroughly heated to a red heat during distillation. It kindles easily and makes an excellent smokeless fuel. An analysis of the coke obtained above is as follows:

*Analysis of coal-tar coke.*

	Per cent.
Moisture <sup>17</sup> .....	1.0
Volatile .....	2.0
Fixed carbon .....	96.5
Ash .....	.5
	100.0

The preferred way to manufacture coke from tar seems to consist of distilling tar to a hard pitch in the usual way and then running the pitch into carbonizing stills, which may be cast-iron or refractory ovens, where the distillation is continued to coke. Wrought-iron or steel-steel stills buckle and deteriorate rapidly.

The experimental tar still used for distilling and coking tar in the laboratory is shown in figure 11. It is made of pipe and fittings and can be assembled readily or taken apart and cleaned. Almost any size of screw pipe may be used in making such a still, although 3, 4, or 6 inch pipe seems to be best. The offtake pipe should not be less than one-half inch in diameter. Gas burners of the Bunsen type are satisfactory for heating.

In using this apparatus allowance must be made for frothing; therefore the still should be filled only about one-half or two-thirds full of the tar. The temperature should be raised slowly, particu-

<sup>17</sup> Moisture could not have been present in the coke as made.

larly until all the water has distilled. During the early stages of distillation the delivery pipe may have to be cooled slightly to condense the low-boiling oils. A condenser is not necessary, however, unless the rate of distillation is very rapid and the tar contains considerable water or a high percentage of low-boiling oils.

Do not permit the offtake pipe to become cold enough to permit congealing of the naphthalene and anthracene fractions. It is necessary to warm the offtake or delivery pipe during the latter part of the distillation to prevent plugging by the congealing of high-boiling fractions. It is well to use a shield of sheet asbestos over the top of the still during distillation.

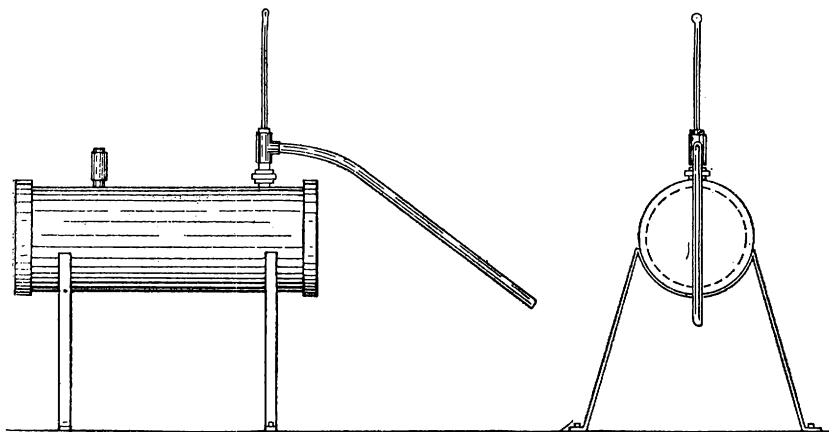


FIGURE 11.—Simple experimental tar still made from pipe and fittings.

### WATER-GAS TAR.

In the manufacture of water gas, wherein coke is the main generator fuel, the tar that is produced is entirely a result of the cracking of mineral oil in hot carbureting or checker chambers. The quality and quantity of tar thus produced depend chiefly on the kind and quality of oil used, the temperature in the carbureting chambers, the length of time the oil vapor is in contact with the hot brickwork in the carbureting chambers, and on the atmosphere in which the oil is cracked. Obviously, then, when all kinds of oils are used separately for this purpose, many different grades of tar will be produced. Therefore it is unjust to condemn water-gas tar for certain purposes until full information on the tar is obtained.

Water-gas tars ordinarily have a low specific gravity and contain very little free carbon. Paraffins are nearly always present, frequently in rather large proportions, whereas phenols, tar acids, are present only as traces, if at all.

For many uses to which coal tar and its products are put, water-gas tar and its products are apparently unsuitable, but they should not

be condemned for all purposes requiring a tar or tar product. Standards giving a tar its high value have changed from time to time and will probably change more. At one time it was thought that carbo-lic acid in coal tar and in heavy oil made these materials particularly valuable for wood preserving; now it is recognized that phenol does not exist in wood very long after treatment. Likewise, the low free-carbon content of water-gas tar was considered detrimental, but many high-grade by-product coke-oven tars have a still lower average content of free carbon. Some investigators have reported water-gas tars as containing no paraffins, bases, or phenols and little free carbon. The wide variations in important properties existing between water-gas tars made with the various oils no doubt occasions much of the discrimination against water-gas tar. However, it may be said of water-gas tars in general that they are separated from water with difficulty; their pitch is small, easily fusible, and readily affected by temperature changes; they contain paraffins, whose presence increases the difficulty of recovering anthracene, and phenols in minute quantities; and their free carbon content is very low. These tars are used as liquid fuel, for "cutting back" coal-tar pitch to make liquid fuel, for the preparation of waterproofing paints, for road tars, and as fuel for Diesel engines.

The waterproofing qualities and low free-carbon content of water-gas tar would seem to make it very suitable for mixing with coal-tar creosote in preparing wood-preserving oil. Nevertheless its exclusion from such products is usually specified.

In some parts of the country where bituminous coal is used as fuel in water-gas generators the tars produced have still different properties. They are heavy, very viscous, easily separated from water, yield as much pitch as coal tar, and contain as much free carbon as coke-oven tar, or more.

Uniform methods of operation with coal fuel have not yet been adopted, hence a "blanket" recommendation or condemnation of all such tars can not be given.

Table 10 gives analyses of water-gas tars from coal and from coke fuel.

TABLE 10.—*Principal differences in the composition of various water-gas tars.*

	Sample 1.	Sample 2.	Sample 3.
Method of operating.....	Without blow run.	With blow run.	Coke.
Fuel used.....	Bituminous coal.	Bituminous coal.	Regular.
Sp. gr. at 15.5° C.....	1.17	1.16	1.055
Free carbon..... per cent.	9.14	4.85	Trace.
Moisture..... do.	8.40	3.00	3.00

*Distillation of dry tar.<sup>a</sup>*

Up to 110° C.....	0.0	0.0	0.2
110 to 170° C.....	.8	.0	1.2
170 to 235° C.....	4.3	1.6	15.7
235 to 270° C.....	9.8	7.2	18.7
270 to 300° C.....	15.3	9.1	20.6
Residue.....	<sup>b</sup> 69.4	82.0	<sup>b</sup> 38.8
Undetermined.....	.4	.1	4.8
Total.....	100.0	100.0	100.0
Tar acids, per cent.....	Trace.	.0	.6

<sup>a</sup> The distillations were made in a 500 c. c. glass distillation flask, with the thermometer bulb at the off-take arm.

<sup>b</sup> Brittle.

A demand for some of these heavy water-gas tars from bituminous coal as a road tar would probably arise if their properties were more generally known. Very little information is available on such tars, and to the writer's knowledge only a few different oils have been employed for carbureting. How wide will be the variety of tars when different gas oils are employed under different operating conditions remains to be seen.

**COST AND YIELDS.**

Operating costs only are considered here. In deriving them certain assumptions are made, these being based on actual conditions in operating plants. It is obvious that costs are lower in a large than in a small plant, for the efficiency usually is greater and fuel economies are made that are impossible in small works. In a small plant with a 6-ton coal-fired tar still where coal costs \$4 a ton delivered and tar 5 cents a gallon, the actual plant costs for labor and materials will be approximately as follows:

*Costs at a small tar distillery.*

Tar distilled per day—1,200 gallons (12,000 pounds), at 5 cents per gallon.....	\$60. 00
Fuel for still—1 ton of coal, at \$4 per ton.....	4. 00
Fuel for boiler— $\frac{1}{2}$ ton of coal, at \$4 per ton.....	2. 00
Labor—engineer and helper.....	10. 00
Total plant costs.....	76. 00

The yield from distilling 1,200 gallons of coal tar is approximately as follows:

*Distillation products from 1,200 gallons of coal tar.*

	Approximate yield.	Approximate specific gravity.
	Gallons.	
Water and loss.....	35	
Crude naphtha.....	25	0.915
Light oil.....	50	.985
Carbolic oil.....	60	1.015
Creosote to a medium soft pitch.....	190	1.05
Pitch (8,940 pounds).....	840	
Total.....	1,200	

The average cost of oil and pitch per gallon is, then,  $\$76.00 \div 1,165$ , or  $6\frac{1}{2}$  cents. Pitch is usually sold by the ton or by the pound, and consequently the cost computed is  $\$12.21$  per ton of 2,000 pounds. Although this is the cost of pitch in bulk, the cost in open-head barrels is not appreciably greater, for tar is usually sold on the basis of gross weight, including the container.

The costs of the paints, stains, disinfectants, road tars, and other tar products discussed in this paper can readily be calculated from the above statement by making proper allowances for the steam, fuel, and labor required in their preparation.

Overhead expenses, repairs and maintenance, and other fixed costs are not included in the figures presented here, as they are not the same in any two plants.

TABLE 11.—*Fractionation of coal tar and some refined and intermediate products obtained.*

First crude distillation of dry tar.	Light oil.	Middle oil (carbolic oil).	Heavy oil (creosote oil and anthracene oil).	Pitch.
Distillation temperatures.	Up to 200 or 210° C.	210 to 240° C.	240 to approximately 315° C.	Above 315° C.
Percentage in tar.	Approximately 5 to 10 per cent by volume.	Approximately 5 to 10 per cent by volume.	Approximately 20 to 30 per cent by volume.	50 to 70 per cent by volume.
Crude commercial products and their uses.	Benzol, solvent naphtha, motor fuel, solvents.	Creosote oil.		Pitch cement, paints.
Intermediate products by washing and distillation or by expression.	Benzene, toluene, xylene.	Crude carbolic acid, disinfectants.	Road oil, wood-preserving oil.	Soft, medium, or hard pitch, coke.
Intermediate chemical products.	Nitro-benzene, aniline salts, aniline oil.	Phenol, naphthalene, heavy hydrocarbons, cresol.	Cresol, naphthalene, anthracene, heavy hydrocarbons.	
Refined chemical products and their uses.	Nitrotoluene and other ingredients of explosives, aniline dyes, hydroquinone and other photographic developers, drugs, medicines.	Carbolic acid, picrates, phthalic acid, naphthols, naphthylamine, salicylic acid.	Anthraquinone, alizarin.	
		Picric acid, picrates, and other nitrocompounds for explosives; naphthol dyes and colors; artificial indigo; refined carbolic acid.	Alizarin dyes.	

### VALUATION OF COAL TAR.

The price that the distiller must pay for coal tar is a matter that is not always under his control, but the relative value of tars at the same price or at different prices is something he must decide, particularly when tar can be obtained from many sources and the supply is greater than the demand. The tar that is most valuable to a distiller in one place might not be exceptionally valuable to a distiller in another place, because the demand for certain tar products is not the same throughout the country. For example, a tar that yields much pitch is perhaps not considered as very high grade, particularly

in places where the market for pitch is poor, but in districts where pitch is in demand and tar oils are not, such a tar might be considered most favorably. Other factors of this nature must be considered in purchasing tar. When many products are prepared from tar, a laboratory analysis is necessary in assigning a proper value to a given tar, and even then the problem may not be so simple as in the example cited.

### TESTING AND GRADING TAR AND TAR PRODUCTS.

Numerous methods of testing coal tar and its derivatives, some of which are recognized as standard for products used for a definite purpose, have been drawn up by various engineers, chemists, societies, and committees. A series developed by the Barrett Co. has been published in the *Journal of Industrial and Engineering Chemistry*.<sup>18</sup> The method to be pursued in any particular case in testing, classifying, and grading tar products is frequently prescribed in the specifications for the particular products. Some of these special methods are given in other government publications, including those mentioned on pages 78 and 79. The tar tests which are most frequently made determine the specific gravity of the tar, the percentage of water present, the percentage of and character of the various fractions obtained on distilling the tar, the percentage of residue on distilling the tar, the nature and consistence of distillation residue, the melting point of distillation residue, and the percentage of free carbon present.

Some of the foregoing tests are also made on the crude tar products, with additional tests which determine principally the percentage of solids at a given temperature, the percentage of naphthalene, the percentage of tar acids, the percentage of unsaturated compounds, the distillation range, color, odor, boiling point, physical appearance, viscosity, and flash point.

### CONCLUSION.

In this bulletin the author has endeavored to discuss tar products in a general way. The yields and properties of the distillate fractions and residues from tar will, of course, vary with the kind and quality of tar distilled. For example, the distillate fractions from tar, particularly from a low-temperature tar, may represent a greater percentage of the original tar than is shown herein, and vice versa. Likewise, the price of tar is not fixed. Costs of all commodities are

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<sup>18</sup> Weiss, J. M., *Methods of analysis used in the coal-tar industry*: *Jour. Ind. and Eng. Chem.*, vol. 10, 1918, Part I, Crude tars, pp. 732-738; Part II, Distilled tars and pitches, pp. 817-823; Part III, Heavy and middle oils, pp. 911-916; Part IV, Benzols and light oils, pp. 1006-1012.

changing so rapidly that definite prices can not be given for the various tars. The price of coal tar once ranged from 3 to 4 cents a gallon and that of water-gas tar from 1 to 2 cents a gallon. In general, these prices do not exist at present (1921) except in long-time contracts that have not expired. Water-gas tar which was at one time considered next to worthless now commands a fair price.

### PUBLICATIONS ON THE UTILIZATION OF COAL.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications can not be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines.

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#### PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

**BULLETIN 40.** The smokeless combustion of coal in boiler furnaces, with a chapter on central heating plants, by D. T. Randall and H. W. Weeks. 1912. 188 pp., 40 figs.

**BULLETIN 58.** Fuel briquetting investigations, July, 1904, to July, 1912, by C. A. Wright. 1913. 277 pp., 21 pls., 3 figs.

**BULLETIN 116.** Methods of sampling delivered coal, and specifications for the purchase of coal for the Government, by G. S. Pope. 1916. 64 pp., 5 pls., 2 figs.

**TECHNICAL PAPER 9.** The status of the gas producer and of the Internal-combustion engine in the utilization of fuels, by R. H. Fernald. 1912. 42 pp. 6 figs.

**TECHNICAL PAPER 50.** Metallurgical coke, by A. W. Belden. 1913. 48 pp., 1 pl., 23 figs.

**TECHNICAL PAPER 80.** Hand firing soft coal under power-plant boilers, by Henry Kreisinger. 1915. 83 pp., 32 figs.

**TECHNICAL PAPER 89.** Coal-tar products and the possibility of increasing their manufacture in the United States, by H. C. Porter, with a chapter on coal-tar products used in explosives, by C. G. Storm. 1915. 21 pp.

**TECHNICAL PAPER 123.** Notes on the uses of low-grade fuel in Europe, by R. H. Fernald. 1915. 37 pp., 4 pls., 4 figs.

**TECHNICAL PAPER 137.** Combustion in the fuel bed of hand-fired furnaces, by Henry Kreisinger, F. K. Ovtz, and C. E. Augustine. 1916. 76 pp., 2 pls., 21 figs.



TECHNICAL PAPER 139. Low-rate combustion in fuel beds of hand-fired furnaces, by Henry Kreisinger, C. E. Augustine, and S. H. Katz. 1918. 52 pp., 9 figs.

TECHNICAL PAPER 180. Firing bituminous coals in large house-heating boilers, by S. B. Flagg. 1917. 22 pp., 1 pl., 16 figs.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 23. Steaming tests of coals and related investigations, September 1, 1904, to December 31, 1908, by L. P. Breckenridge, Henry Kreisinger, and W. T. Ray. 1912. 380 pp., 2 pls., 94 figs. 50 cents.

BULLETIN 24. Binders for coal briquettes, by J. E. Mills. 1911. 56 pp. 1 fig. 5 cents.

BULLETIN 27. Tests of coal and briquettes as fuel for house-heating boilers by D. T. Randall. 1911. 44 pp. 10 cents.

BULLETIN 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 1911. 33 pp., 9 figs. 5 cents.

BULLETIN 37. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests, and some foreign specifications for briquetted fuel, by W. F. M. Goss. 1911. 58 pp., 4 pls., 35 figs. 15 cents.

BULLETIN 138. Coking of Illinois coal, by F. K. Ovitz. 1917. 71 pp., 11 pls., 1 fig. 20 cents.

TECHNICAL PAPER 63. Factors governing the combustion of coal in boiler furnaces, a preliminary report, by J. K. Clement, J. C. W. Frazer, and C. E. Augustine. 1914. 46 pp., 26 figs. 10 cents.

TECHNICAL PAPER 183. New views of the combustion of the volatile matter in coal, by S. H. Katz. 1917. 15 pp., 1 fig. 5 cents.

TECHNICAL PAPER 195. The tars distilled from bituminous coal in hand-fired furnaces, by S. Katz. 1918. 20 pp., 2 pls., 3 figs. 5 cents.



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