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"ASPECTS AND PROSPECTS -- CRESOLS AND
CRESYLIC ACIDS"

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INTRODUCTION

When I was asked to make this talk, I was told to choose my subject and since the tar acids, other than phenol, have not been covered separately in any of your previous meetings, I decided upon them as my subject. It must be pointed out, however, that the title of this paper is deceiving if it is supposed that equal time is to be devoted to both "aspects" and "prospects." The subject of the past and present is so much more certain than that of the future, that "prospects" are relegated to a minor position and emphasis is placed upon the "aspects" portion.

PROLOGUE

All of you who operate coke ovens are producers of tar acids, even though your tar is not treated by you for removal of acids. If you sell chemical oil, the price you derive is probably partially dependent upon the tar acid market, and if you sell tar, the revenue that can be obtained by your buyers is somewhat dependent upon market prices for their acids, if they remove chemicals from the tar. Therefore, the subject should be of some interest to all coke oven operators. With this thought in mind certain facts will be outlined which may not be familiar to most of you at this time. Certainly, the subject is a vast one and one not well understood by many segments of industry, and it most certainly cannot be fully treated in one session.

DEFINITION

Tar acids in this discussion will be the collective nomenclature used for benzo phenol, the three cresols or ortho, meta and para methyl phenols, the six xylenols or di methyl phenols, the ethyl phenols, propyl phenols, tri methyl phenols and all of the other acids so called because they react with caustic soda to form phenolate, cresylates and sodium compounds of higher boiling acids, thereby being of acid nature, even though only weakly acid. Forty different tar acids have been found in coal tar, and petroleum distillates probably contain others more complicated chemically. Nine of the twenty found in coal tar boiling below 230°C . are the important ones of commerce, although some higher boiling ones have limited industrial uses. The nine most widely utilized acids are phenol, boiling at 181.4°C .; ortho cresol, boiling at 190.8°C .; meta and para cresols, boiling at 202.8°C ., and 202.3°C ., respectively; 2.5 xyleneol and 2.4 xyleneol, each boiling at 211.5°C .; 2.3 xyleneol, boiling point 218°C . 3.5 xyleneol, boiling point 219.5°C .; and 3.4 xyleneol, boiling point 225°C ., (7). The numbers refer to the position of the methyl groups in the benzol ring, considering the hydroxy group of phenol as in position number one. There are eleven other acids boiling below 230°C ., found in coal tar including, 2.6 xyleneol, ethyl and propyl phenols and ethyl cresols, but none boil below 204°C .

HISTORY

Prior to the first world war, tar acids were produced in very limited quantities in this country and any grade that domestic consumers required could be imported from abroad. The primary demand then was for disinfectants and soaps and for solvent purposes, although acids left in oils found use for flotation of ores. The supply was so inadequate during the war that as a consequence production

was increased by the one potentially large manufacturer and this supply continued after the war. The foreign producers, however, could then export all grades to this country and, in spite of increased consumption, because of expanding resin demand, domestic producers had difficulty in meeting foreign competition and getting business. A duty was granted in 1922, the Fordney McCumber one, on coal tar distillates containing tar acids, and this was worded so that tar acids distilling less than 75 percent at 215°C and not more than 5 percent at 190°C by straight run distillation methods, were duty free. Any acids showing more than 5 percent distilled over at 190°C and (or) more than 75 percent distilled over at 215°C were dutiable at 40 percent of the ad valorem American valuation plus 7 cents per pound. This rate was prohibitive for the imported acids of the kind generally required and domestic producers were then able to sell their outputs. The high boiling acids were not dutiable if they distilled less than 75 percent at 215°C. and importations of these increased enormously. They were permitted to be duty free, because the United States needed them for high coefficient disinfectants at that time. It was then that they began to be called cresylic acids, whereas before that time, lower boiling acids had been called cresylic acids and in that duty free higher boiling distillation range, acids had been called high boiling or high coefficient acid.

The demand for tar acids continued to expand for plasticizers, resins and all regular uses and domestic production was insufficient, therefore, several new producers entered the field. One started operations in 1928, two others began in 1929, and another started in 1930. Late in 1929 demand receded, two of the new producers dismantled their plants, and competition became very keen between the remaining ones. The resin industry continued to expand and in 1936 additional capacity was installed and soon thereafter in the thirties, several new companies began to produce from petroleum distillates.

The high boiling petroleum acids could not be called tar acids or high-boiling tar acids because not derived from tar, therefore, with their advent into the picture, the name cresylic acid began to be used for acid of almost any distillation range, even though many grades contained absolutely no cresol, the word from which cresylic acid is presumed to have been derived. Because prices for low-boiling acids had always been above those for the higher boiling duty free acids, most of the coal tar domestic producers, to protect their interests, began to call any acid, distilling 50 percent off below 204°C., a cresol, if phenol did not predominate and quoted prices by the pound instead of by the gallon, as for cresylic acid. These cresols could, by specification in some instances, contain much xylenol and phenol or could be a very pure mixture of the cresols such as U.S.P. Cresol. The name cresol, with explanatory letters or numbers or combinations of both, became established and the name cresylic acid was used for higher-boiling mixtures. Once an importer attempted to prove that cresylic acid was a mixture of cresols, as defined by textbooks, in order to have the benefit of a lower duty for material he imported. The New York Appraisers insisted, at a legal hearing, that regular practice of producers, as declared by their representatives, was more important than textbook definitions and since the grade imported into this country was called a cresol by domestic producers, duty would have to be paid based on American valuation for a cresol, and not for a cresylic acid.

The demand for tar acids was at the maximum of availability during World War II because of very important end uses and since then the demand has continued to expand until it reached an all-time high in 1955.

PRODUCTION

Coal is never coked for tar or other by-products. It is always coked for either the coke itself or gas. Tar acids from tar are obtained by treating a middle oil or carbolic oil cut in tar distillation; or a "topped" chemical oil cut, where residual tar is being used as fuel, with caustic soda, separating from the oil the layer of sodium cresylate so formed, and steam distilling for removal of impurities. The sodium compounds are then "sprung" by means of carbon dioxide and later treated with sulphuric acid and the liberated free acids are vacuum distilled fractionally. Similar procedure is used to separate petroleum derived acids from their oils. Another source of some of these acids is from waste ammoniacal liquors after removal of ammonium sulphate. These liquors are treated to remove phenol and cresol (mostly ortho cresol) and this mixture is another type of raw material for production of refined tar acids.

The percentage of cresols and cresylic acids varies in tars produced from different coals. It also varies with the temperature and coking time in the same ovens and in the types of ovens used. Just as low temperature tar (approximately maximum 700°C. coking temperature) (1) gives a very large yield of tar acids so also do tars produced in high temperature ovens (approximately 1200°C temperature maximum) when lower temperatures than 1200°C., and longer cycles than normal, are used. If it is assumed that coking capacity in by-product ovens is sufficient for 100 percent steel operations, and no supplementary bee hive ovens are used, when steel operations are at 50 percent of capacity with all ovens still operating, there would probably be as much tar acid yield from the reduced volume of tar as there would be at 100 percent capacity for the ovens. Naphthalene yield, inversely, with steel at 50 percent of capacity, would only be about 25 percent of amount of yield when steel is running 100 percent. Furthermore, the percentage of cresol and xylenol in total acids would rise, with phenol percentage receding, when operations are at a lower rate than maximum. An actual sample analyzed in 1951 as compared to one analyzed in 1953 showed the following difference (2) -

	<u>1951</u>	<u>1953</u>
Phenol	34.5%	29.0%
Ortho cresol	9.0%	9.5%
Meta and para cresols	27.5%	31.5%
Low boiling xylenols	6.5%	8.0%
High boiling xylenols	9.0%	10.5%
High boiling acids, residue and loss	13.5%	11.5%

Phenol percentage is highest when demand for steel is strong whereas, when demand is reduced, cresol volume is highest.

APPLICATION

I know of no other products, used in chemical reactions which are mixtures of as many different chemicals as cresols and cresylic acids. Uniformity in successive shipments, therefore, is of utmost importance and the available mixtures that can be offered are very numerous, from blending of the five to eight or more primary cuts generally made in distillation. These acids are used with one chemical for resins, generally formaldehyde, but sometimes furfural or another aldehyde. For tri-cresyl phosphate they are used with one pure chemical - phosphorus oxychloride or phosphorus pentachloride. With such a situation existing, the sale of these acids is an art and salesmen can profit by experience in both laboratories and plants of producers. The most important use for tar acids is phenolic resins and many grades of cresols and cresylic acids are valuable but, insufficient supplies of some of them, at times, have enabled synthetic phenol to obtain an increasing percentage of total sales. Where meta para cresol would be ideal for varnishes, for instance, a phenol and xylenol mixture can often be used as a substitute and the xylenol imported and sometimes obtainable at prices lower than domestic equivalents. For molding powders, phenol, or phenol and cresol, are generally used.

Curve I shows to what extent cresols and cresylic acids have lost their percentage position with respect to phenol, because supplies were insufficient, despite the continuous increase in availability. About 70 percent of phenol produced is used for synthetic resins. Curve II, for natural and synthetic phenol, shows the terrific increase in volume production almost every year since 1940 with recessions only in the years 1949 and 1952. Natural phenol quantities included in total phenol exceeded 25,000,000 lbs., only in the years, 1944, 1953, and 1955, but exceeded 20,000,000 lbs., in all years except 1942, 1943, 1946, and 1949. Curve I was prepared without including domestic crude cresylic acid figures reported to U. S. Tariff Commission, for material boiling less than 75 percent at 215°C., because separate figures for this type, for fear of disclosures, could not be made available until 1944. The comparison is made for the percentage of all other grades of cresols and cresylic acids, from all other sources, in total tar acids, which include phenol both natural and synthetic. The year 1955 had, by far, the largest total for these acids (approximately 126,000,000 lbs.), but they accounted for only 19.6 percent of the total. The resin uses for acids include plywood glues, molding powders, laminating and insulating varnishes, oil soluble varnishes and shell molding.

Tri-cresyl phosphate used most of the meta-para cresol in World War II for coatings for degaussing cable for vessels to prevent explosions of magnetic mines. Tri-cresyl phosphate is a valuable consumer of meta-para cresol and the xylenols not only for plasticizer use but also for a lead scavenger in gasoline to prevent deposits on spark plugs from tetraethyl lead in the gasoline.

Another important use for meta-para cresol recently has been for 2:6 ditertiary butyl para cresol for an anti-oxidant for transformer and circuit breaking oils, aviation gasoline and edible oils. Butylated metacresol has some outlets for rubber chemicals or can be debutylated to pure meta cresol. As the demand for these three outlets for meta para cresol (generally, 63 percent meta and 37 percent para in high temperature coal tar) increased, some former outlets diminished as, for instance, health soaps and soluble disinfectants, such as Bureau of Animal Industry of U.S.P. Cresol Compounds.

Ortho cresol has had a resin application for years but not a large one, except when left in the 80 or 90 percent phenols produced by natural phenol manufacturers for resins and petroleum refining. Ortho cresol found large outlets twenty to twenty five years ago, when the Duo Sol process of preparation of lubricating oils was first introduced. Later, di-nitro-ortho-cresol, an agricultural insecticide, required all the excess ortho cresol available. The demand for this product has receded and new Duo Sol plants are not being constructed with consequent demand for initial charges. Higher boiling acids such as meta-para cresol and the xylenols are now being used with phenol for existing Duo Sol extraction plants for separation of naphthenes from paraffins. Another use for ortho cresol, which has been diminishing, is for the preparation of coumarin, a flavoring chemical, which has been proven or has been suspected of being a cumulative poison. Ortho cresol is also used for cresotinic acid, used for dyes. No new uses have been successfully developed recently for large-scale use and this cresol now has much less application than supply could satisfy, in pure form, but it can always be utilized in the wider boiling grades of cresylic acids, not for resins or tri cresyl phosphate use. Ortho cresol, the least reactive of the cresols for resins, presents only two reactive positions to formaldehyde as compared to three for meta cresol. Ortho tri-cresyl phosphate if taken internally is poisonous and years ago, was responsible for many cases of paralysis and some deaths.

The xylenols, in combination with cresols or separately, make good resins or tri-xylene phosphate. They are also excellent for the flotation of copper ore in mining, when mixed with phosphorus penta-sulphide. They are used for mercerizing compounds, separately or mixed with cresols and for wool scouring soaps. They are used for wire enamel solvents, engine cleaning compounds, oil additives, and for soluble disinfectants and in combination with higher boiling acids are used to make tar acid oils which are used for sheep dips, for disinfectants of the emulsion types, and for flotation of ores. With phenol considered as one on the germicidal scale and with tests being made on typhoid germs, the cresols have killing power from two to three times that of pure phenol and the xylenols from eight to twelve times as much. Some of the acids, boiling above the xylenols, have killing power forty or fifty times as much as phenol, if properly formulated. The high boiling tar acids mixed with oil have a use for these high coefficient emulsifiable disinfectants when compounded with rosin or castor oil and caustic soda, but supply is in excess of demand and, therefore, prices are relatively low. As the boiling range of these acids goes up, the killing power on germ life increases, and the burning or corrosive effect on the human skin decreases. Phenol is the most corrosive and ortho cresol is more corrosive than the other cresols.

IMPORTED ACIDS

The amounts imported of duty free cresylic acid frequently called A.D.F. (American Duty Free) acid have been very large. The most desirable type for numerous purposes is mostly composed of xylenols and efforts are made to have the 75 percent point in distillation as near to 215°C. as possible. In order to allow a little leeway for safety many exporters try to get close to 67 to 70 percent off in distillation at 215°C., because, if the acid is declared dutiable, the duty of 10 percent on American valuation plus 1 3/4 cents per pound would make purchase prohibitive. This type of acid may contain up to 20 or 30 percent of meta para cresol, but is mostly xyleneol if dry point is appreciably below 230°C., as is generally the case. As the distillation range goes up however, the

cresol content can be increased somewhat. For resins, acid close to the duty free line is most desirable. The distillation test for amount distilled over at 215°C., is very important. The Government, in the late twenties, at one time changed the test method slightly and inadvertently omitted a correction for the emerging stem of the thermometer. This correction should have been included but since it was not, acid arriving at all the different parts was declared to be dutiable. It was not accepted by buyers, because of cost of duty, and sellers could not afford to return it to ports of export. It, therefore, remained on the docks, unliquidated at several ports until a change in the official method of test was approved by Washington and a correction for thermometer emerging stem was inserted in the test method. To give some idea of the large amount of acid entering this country from abroad, Curve III has been drawn. It shows the amounts of duty free acid entering this country from 1940 to 1955. Curve IV shows the percentage of imported duty free acid in total of domestic crude and refined cresols and cresylic acids plus imported duty free acid for the years 1944 to 1955. Years 1940 to 1943 are omitted because no figures are available for crude cresylic acids for these years. Imports were over 34 million pounds in 1951, the highest of all years as shown by the curve. Other peak years exceeding 20 million pounds were 1943, 1946, 1947, 1948, 1950, and 1955. Prior to 1943, the peak year was 1929 (about 18,000,000 lbs.). 1937 imports were almost 17,000,000 lbs. The percentage of imported acids to total acids after 1944 was highest in 1946, 1947, 1948, 1950, and 1951 and since then has always been below 20 percent. With 24,500,000 lbs. coming in during 1955, the percentage of the total was only 15.8 percent. Percentage in 1948 with 25,500,000 lbs., was 23.4 percent.

Sales of imported acid are highest when demand from domestic sources is unsatisfied to the greatest extent. The percentage is surprisingly high in some years and clearly shows the importance of these foreign acids in our domestic consumption. The duty on cresylic acid, distilling 75% or more at 215°C is now 10% of American valuation plus 1 3/4 cents per pound. This rate became effective in 1948. From 1930 to 1948, the rate was 20% plus 3 1/2 cents per pound. The amounts of dutiable acid that have entered this country are small.

GOVERNMENT METHODS OF REPORTING

At this point, and before discussing domestically produced acid, it is advisable to outline what reports the Government receives from industry regarding production each year. Two departments compile the production figures for the various grades of tar acids and a third one records the imported figures. The Bureau of Mines of the Department of the Interior obtains the production statistics for the coke oven operators most of whom are iron and steel producers. These include the steel mills, which have refining equipment for acids. They get reports for cresylic acid produced, all of which is called refined, and the cresols, as (I.) meta-para cresol or meta-para ortho cresol mixtures and as (II) pure ortho, meta or para cresols separated. The U. S. Tariff Commission collects the production figures for tar acids from the tar distillers, which includes companies buying tar or chemical oil for processing to separate its components. Some of these companies operate coke ovens to a limited extent. The tar distillers not only report production of refined cresylic acid; meta-para cresol; meta, para and ortho cresols mixed, and meta, para or ortho cresol pure, but also a type of acid designated as crude cresylic acid. The producers from petroleum sources report to the Tariff Commission also for refined cresylic acid and cresols and crude cresylic acid. The crude cresylic acid reported by the tar distillers and petroleum operators, and which is not reported by the coke oven operators, is not necessarily crude and is not a

raw material for refined cresylic acid, as might be supposed, but instead is quite different chemically. Duty free imported acid, as previously mentioned, is any acid distilling less than 75 percent off at 215°C. The Bureau of the Census of the Commerce Department compiles the figures for this type imported from foreign countries. In order to have a comparison of the amounts of acids produced in this country, which would distill at temperatures as high as duty free acids, the Tariff Commission maintains the records of production of these types of acids under the nomenclature "Crude Cresylic Acid." Such acids are from some sources as free from impurities as the purest mixed cresols. Acids, produced from high temperature coking, contain much less of these high boiling components than do petroleum distillates and much more of what is available is first mixed with cresols or low-boiling xylenols before reporting. As a consequence, any comparative reports of crude cresylic acid produced by tar distillers and petroleum producers give an erroneous impression of relative production of all grades, if the assumption is made that this crude is a source of refined acid. For example, a quantity of 29 million pounds of crude cresylic acid was reported produced in 1955, of which 24½ million pounds or 84.5 percent was of petroleum origin. In that same year, 65,900,000 lbs. of refined cresylic acid were produced and 27,900,000 lbs. of mixed cresols were produced not including any pure cresols, which would include cresol of synthetic origin such as para cresol from toluene. The refined cresylic acid and mixed cresol, but excluding pure cresols, added to the crude cresylic gives a total of 122,800,000 lbs. as the 1955 production. Of this amount 57,332,000 lbs. (crude and refined) was of petroleum origin, assuming none of the crude is sold, reworked, and later reported as refined. The percentage from petroleum sources was, therefore, approximately 47 percent and not 84.5 percent as might be expected if only crude figures are used, and it is assumed that refined cresylic acids and cresols are obtained from the total crude cresylic acid, as crude naphthalene for example, is made into refined. If benzo-phenol from coal tar and petroleum operations were to be included in this calculation, the percentage of tar acid from petroleum would be much lower, because, in 1955, phenol from coal tar distillates was 37,866,600 lbs., as compared to 3,810,000 lbs., from petroleum. These figures are emphasized, because a recent copy of an important magazine (3) in giving percentages of light oils produced from petroleum included the statement that 84 percent of the cresylic acid made in 1955 was supplied by the petroleum industry.

DOMESTICALLY PRODUCED ACIDS

Cresols reported by the coal tar and petroleum producers increased vastly in volume in recent years as shown by Curve V. In 1948 the volume reached its peak up to that time; then a further peak in 1951 and finally higher than ever before in 1955. Indications are that the 1956 volume will be less than in 1955, but cresylic acid will probably be more. Final reports for 1956 are not yet available. For sales purposes, cresylic acids may be increased in production and cresols may be decreased or VICE VERSA in successive years depending upon the demand and available supply. Volume can only be truly compared by adding cresol and cresylic acid figures together. For example, one year may encounter a strong demand for a tri cresyl phosphate grade with seventy percent meta-para cresol, as offered by some producers. This is called cresylic acid because temperature, by specification, is not less than 240°C. when 50 percent is distilled off. Another year may develop a strong demand for a resin grade with only 65 percent meta para cresol, but because of ortho cresol and phenol content, the 50 percent off point in distillation will be below 204°C. by specification. Such a grade would be called a cresol by some producers. The cresol production curve includes synthetic para cresol, but it is only a small percentage of the total.

Curve VI is for both petroleum and coal tar refined cresylic acid. If the coke oven producers prepared and sold cresylic acid distilling less than 75 percent off at 215°C., this acid is included in figures used for this curve but acid distilling less than 75 percent at 215°C., is not included in figures if made by petroleum or tar distillers. Some material might be included in figures for this curve from companies who do not use the same dividing lines as other companies for differentiating between cresols and cresylic acids, but successive reports would be expected to be consistent. The first production peak was in 1943, and the volume of that year was not attained again until 1951, but each year since excepting 1954, volume has risen until an all-time peak was reached in 1955. Eleven months for 1956 show a thirteen percent higher figure than the same eleven months for 1955, therefore, an all-time high is to be expected for 1956.

Curve VII for crude cresylic acid includes reports from tar distillers and petroleum distillers only, distillation 75 percent off not below 215°C. Nineteen companies are now reporting production of cresylic acid, all grades, but only ten of them are included in the data for Curve VII. This grade, first reported separately in 1944, reached its greatest peak in 1947, probably because some new producers that year did not separate the lower boiling fractions shown on the refined cresylic acid curve. Since 1952, production has increased every year with 1955 the peak year.

QUALITY

Probably the most important item regarding the quality of tar acids is uniformity in successive shipments. After a grade has been adopted and specifications established for its derivatives, buyers want later shipments the same chemically and there is no one means of maintaining the uniformity as perfectly as by giving uniformity in distillation range. If for each five degrees or ten degrees in the distillation, percentage distilled off is very close to that of previous shipments by straight run distillation and the crudes come from the same sources as for previous shipments, good uniformity of constituents can be expected. If, however, low temperature coking distillates or petroleum distillates are mixed with high temperature coking acids, for example, whereas formerly they were not mixed, the meta-para ratio could be changed or the 2.4 and 2.5 xylenol ratio could vary and other chemical constituents might be different, even if distillation were uniform. Straight run distillation is a test that can be run quickly, is one often used in operation of stills for separating the different cuts, and is the test used to determine dutiability of imported acids. It does not give percentage of different cresols or xylenols or percentages of mixtures distilling at the same temperature, as would be obtained from fractional distillation, but fractional distillation takes much more time to perform.

As a check upon distillation guarantees, some acids can be determined accurately in acid mixtures by analytical methods. Phenol or ortho cresol in pure form can be tested by melting point but in mixtures, the Chapin Colorimetric test for phenol and the cineole method for ortho cresol are very accurate. Meta cresol can be determined by trinitration of meta-para cresol and para cresol can be determined by difference after establishing total meta-para cresol content by fractional distillation. Accurate tests for individual xylenols in complex mixtures are not available. Specific gravity is also a good check for uniformity. As the boiling range of the acid rises, the gravity of the acid recedes.

Having established uniformity of essential ingredients, impurities should be carefully assayed. At one time a tar acid content of from 97 to 99 percent was acceptable but in more recent years, most of the acids are furnished with tar acid content exceeding 99 percent. Of the impurities always present, water is objectionable because no purchaser wants to pay for water and also because for some uses, notably tri-cresol phosphate, it lowers the yield. If all impurities combined are restricted from exceeding one percent, probably water content is permitted up to half of one percent, but some industries demand less. In coal tar acids, pyridine bases and naphthalene and neutral oils are the naturally occurring impurities, but careful preparation can keep these down to very low percentages. Both petroleum and coal tar acids are generally contaminated with some sulphur compounds, which for many purposes, are very objectionable and extensive efforts are made to remove them. Even laboratory methods, for accurate determination of sulphur percentage, are long and tedious.

The very evident characteristics of tar acids, much discussed by buyers and sellers, are color and odor. Generally, the refined acids leave the stills water white, but even before cooling will develop a pinkish or yellowish color. If exposed to light or air, oxidation darkens these to straw, red or brown colors, whereas pale pink or yellow can be maintained in closed containers in the dark. Redistillation will lighten a dark color, because of chemical reduction and will cause removal of some of the dyes, and thus permit color to remain light for a longer time, after a redistillation, but the traces of dyes which cause the colors, will eventually again cause darkening upon oxidation. High sulphur content, due to the reducing action of sulphur compounds, will sometimes cause light colors to be more permanent. Acids are occasionally purple or green or blue but none of these colors are necessarily detrimental for resin or plasticizer derivatives, and actual acceptability can only be determined by laboratory synthesis of products to be made.

Odors of acids are not only characteristic of their chemical constituents, but sulphur or other impurity contamination, makes them very obnoxious for certain uses. Some volatile sulphur compounds, such as hydrogensulphide, can be removed by dry air blowing, but the thio compounds cannot be easily removed. For many purposes, foul odors are objectionable, particularly for disinfectants and resins. They are described all the way from smoky, naphthalene, pyridine, etc., to rotten eggs, onion, down draft in coal burning chimneys on wet days and mercaptan, which is actually nauseating. A clean phenolic or cresolic odor is not unpleasant, nor is the less penetrating somewhat burnt odor of the higher boiling acids. Many purchases have been made for soap purposes on odor alone. Even traces of naphthalene or pyridine can be detected by odor, by combining the acid content with caustic soda and smelling the resulting sodium compound. This odor gives a good indication of purity, because experience makes it possible to guess percentage of naphthalene or pyridine present, if small, and analytical tests can confirm exact percentages present.

FUTURE

Cresols and cresylic acids have had so many important roles in our chemical progress, both in peace and war, since World War I that it seems safe to predict that a strong demand will continue. As soon as one use diminishes, as for example, health soaps, another one surges forward as, for example, di butyl-para cresol. As one resin use recedes, another one seems to increase. When there is shortage of domestic coal tar acid, especially when there are steel or labor strikes, the petroleum industry may be expected to offer larger volumes and the foreigners will sell larger amounts in this country. Inversely, when

the production of domestic acid is large, the importers will expect to sell less foreign acid in this country. The European manufacturers have never seemed to have a large demand for acids of the A.D.F. specification in their countries excepting for symmetrical xylenol, partially because they have saved such acid for export to this country and, also, because they generally obtained a higher price in this country. The lower boiling more desirable grades for most purposes, produced at the same time that A.D.F. grades are made, could then be used locally or exported to other countries where there is no or but little import duty. The United States has never been an exporter of many tar acids, besides synthetic phenol and foreign producers have supplied the world, generally speaking.

It has been stated that maximum potential amount of petroleum cresylic acid is 77,000,000 lbs. (4) and that petroleum cresylic has "an uncertain present and a still more uncertain future." (5) To the contrary it should be stated that two petroleum refiners are reported to be expanding their capacity, (6) and that this maximum may soon be attained or even exceeded. Production in 1955 was 37,000,000 pounds refined cresylic acid and separated phenol and 24,500,000 pounds crude cresylic acid, previously explained as high boiling. Some of this high boiling acid may have been refractionated and the separated lower boiling grade reported as refined cresylic. Coal tar cresol and cresylic acid total in 1955 was 65,500,000 pounds and phenol was 38,000,000 pounds. In addition, 7,700,000 pounds of pure cresols were mostly from coal tar origin. Dutiable imports were 400,000 pounds and duty free imports were 24,500,000 pounds making a total for the year of 197,600,000 pounds from non-synthetic origin excepting a small amount of synthetic para cresol. It is probable that even more high boiling fractions could have been made available if they could have been sold, but the amount of the lower boiling grades were just about at a maximum. There is no assurance that less tar will be burned by the steel mills without processing, therefore, larger coal tar potential does not seem to be certain. While more coke ovens will be erected, as steel output expands and older ovens wear out, there is always the probability that more oxygen will be used in the smelting of the iron ore with consequent decrease in the amount of coke necessary. Accordingly, it is not believed that we can hope for large increases in tar acids in this country from high temperature coking. The yield of tar acids is so very much higher from low temperature coking that this process may, and probably will, give us increased production, if it can be worked out to be profitable. It could certainly be expected to furnish cresols at a lower price than they could be offered, if of synthetic origin. The large potential for the future is for cresols from hydrogenation of coal, but the necessary tremendous investment may not be undertaken until a real shortage of petroleum fuel develops. Such a process could never be considered for its tar acid production alone although yield per ton of coal is said to be many times as much as from high temperature coking.

Another important source of tar acids at some future date may be from oil shale which is available in large quantities in Colorado. The shale known to be there should produce 80 to 100 billion barrels (4) of distillate it is estimated and tar acid yield would be good. There seems to be no certainty of any regular great increase in volume from any source, compared to 1955. Even if petroleum produced 77 to 80 million pounds as compared to 61,000,000 pounds in 1955 and if all the coal tar was processed to extract acids before burning or using for other purposes, thus giving possibly 25,000,000 pounds more and if as much A.D.F. acid were imported regularly, as in 1951, there would still be only about 250,000,000 pounds, of which about 50,000,000 pounds would be phenol, leaving 200,000,000 pounds of cresols and cresylic acids.

Some of this could not be used for the chemical purposes for which cresols and xylenols are so very important and for which shortage might become acute.

Currently, the best prospects appear to be from low temperature coking and from more petroleum acid, than the 77,000,000 pounds previously cited as maximum. 1956 demand was not quite as good as 1955 for pure and mixed cresols and possibly more time will elapse before demand will require more than present availability.

Certainly the history of this country has been that when something was in short supply, production was expanded or a satisfactory substitute provided. This has been proven to be true for tar acids in the form of phenol, closely related to cresol. From the numerous possibilities outlined, a solution of the problem is to be expected when demand warrants increased volume.

It is nice to have had this opportunity to outline these reminiscences of my experience in connection with marketing tar acids and it is hoped that some thoughts will be forthcoming to some of you, which will further the progress of tar acids in the future economic picture.