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Problems of dephenolization of waste liquors

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More or less concentrated ammoniacal liquors are originating from low or high temperature carbonization of solid fuels, from hydrogenation of coal, from gasification of solid fuels, etc. With an increased amount of solid fuels processed the disposal of the large volumes of waste liquor became a major problem of the coal processing industry. In addition the vast volumes of such type of liquors has led to a rising demand that additional pollution of rivers and lakes be prohibited and that existing conditions be improved. Especially the phenol content of the waste water is highly objectionable if the wastes are discharged into a stream because phenols impart penetrating tastes to drinking water after chlorination and are able to destroy the fish life in rivers and lakes. When carbonizing brown coal and lignite, besides mono- and polyhydric phenols and fatty acids, alcohols, aldehydes, ketenes, amines, pyridines and other organic substances are present in the waste liquor. Heretofore in many cases the phenols have been extracted from the waste liquors before their disposal, whereas almost no efforts have been made to recover other organic compounds. However, it must be kept in mind that the selling price of the recovered phenols does not cover the expenditures which must be spent for their extraction.

In the Ruhr district the "Emscher Genossenschaft" was chiefly responsible for the quality of the drinking water and supervised therefore rigidly the composition of the discharged wastes. Because the phenol extraction was not economical a somewhat peculiar system was set up. The "Emscher Genossenschaft" erected dephenolization plants at their own expense, the coke plants operated the extraction plants and were refunded for their operating expenditures and delivered the recovered phenols to the Emscher Genossenschaft which acted as selling agency.

The following figures were published in 1938:

Revenues:	
phenols sold	RM 1,079,684.96
phenols stored	" 55,138.72
	" 1,134,823.68
Expenditures	
Operation, maintenance	
Administration	RM 929,556.29
Taxes	" 21,497.63
Interest, depreciation	" 333,769.65
	RM 1,284,823.57
Revenues	RM 1,134,823.68
Expenditures	" 1,284,823.57
Losses in 1938	RM 149,999.89

Despite considerable annual losses the plants were operated continuously. The preceding figures show very clearly that all efforts were made to improve the economy of the employed processes.

The following article contains a short description of several processes and the author's experience from practical operation of dephenolization plants as well as the results of scientific investigations which were carried out by the author and one of his assistants.

#### A. Practical operation of dephenolization plants

Processes which have been employed either to dispose of or to recover the phenols from waste liquors can be divided into

- a) processes which intend to destroy the phenols in order to keep them away from streams and lakes

b) adsorption processes

c) extraction processes

d) distillation processes

a) A very simple method to dispose of the phenols seems to be the vaporization of the liquor and to discharge the phenol containing water steam into the atmosphere. Ordinarily the incandescent coke after having been transferred from the coke oven chamber to the quencher car is quenched by water. Due to the heat content of the coke considerable amounts of water are vaporized and the water steam is discharged into the atmosphere. Replacing the usually employed fresh water by waste liquor seems to be a simple method to dispose of at least part of the wastes. However, the color of the coke is affected by the content of organic and inorganic substances of the waste liquor, the useful life of the quencher car and the steel work of the quenching tower is greatly reduced and the plant apparatus is attacked. Since the phenols are not decomposed during the quenching operation but merely vaporized or entrained in the water steam, part of them is deposited on neighboring ground, damaging the plant life and eventually reaching the rivers. For those reasons the method has been abandoned. It has been further proposed to admit the waste liquor in a stack so that it is vaporized by the sensible heat of the flue gases. However, in order to prevent destruction of the steel or brickwork from which the stack is built any condensation of the introduced liquor must be carefully prevented. The amount of liquor which can be vaporized per volume of flue gas depends on the flue gas temperature and the dewpoint of the gas from the top of the stack. As pointed out before, a considerable percentage of the phenols will be deposited on the adjacent ground. Vaporization methods cannot solve the problems to protect the atmosphere or the rivers from being polluted by phenols.

The biological Nolte process claims to be able to decompose the phenols by means of bacteria which are feeding on phenols. However, the liquors must be diluted due to the fact that the bacteria will digest only low concentrations of phenols. The plant consists of a system of concrete channels through which the diluted liquor is passed, air is admitted to the solution by means of an undershot wheel. By the action of the bacteria and the air the phenols are decomposed. Great experience is required for the proper operation of the process because for unknown reasons the bacteria are sometimes poisoned, serious formation of foams was observed so that a discharge of the purified liquor became almost impossible. But a few plants of this type were constructed mostly in connection with a preceding phenol extraction plant which had already removed 80 - 90% of the phenols. The Nolte process should be considered only as a supplement to another process if a waste liquor of extremely low phenol content is required.

b) Like other hydrocarbons phenols can be adsorbed by means of active solid materials such as activated carbon, etc. In order to bring down the phenol content of an already treated waste liquor, the latter was passed through a filter bed consisting of ash and blow over dust which results from the gasification of brown coal by means of "Winkler producers". The small particles of active brown coal coke will easily adsorb phenols from the liquor before the latter is discharged into a stream or the ground. However, no phenols can be recovered by the application of this method and the exhausted ash must be dumped. In order to recover phenols from the wastes they were passed through beds of activated carbon whereafter the adsorbed phenols were extracted from the coal by means of benzol. A commercial plant of this type was operated in the Ruhr area but had to be shut down due to operating difficulties. Since tar oils which are always present in the wastes are adsorbed from the activated carbon as easily as the

phenols, the liquor, prior to its admission in the filters, had to be liberated from oils and tar. The liquor was first passed through two tar absorbers the bottom of which was filled with tar above which steel turnings were supported between perforated plates. The liquor was further led through a layer of coke in a third vessel. The cleaned liquor was preheated and admitted to the adsorbers which were filled with activated carbon. A fresh adsorber removes over 99% of the phenol. The adsorbed phenol was removed from the coal by washing with warm benzol. As soon as the phenol was extracted, the benzol was drained from the adsorber and the still remaining benzol vaporized with steam. The benzol-phenol solution was distilled whereby the phenol remained in the still. Practical operation proved that despite the rather extended pretreating system tar oils were deposited in the pores of the adsorbent, thus reducing its efficiency and increasing the consumption of the active carbon. It sometimes happened that the content of an opened adsorber ignited, endangering the whole plant. Due to the various difficulties encountered in the operation of the plant the latter was shut down and no further plant of this type was constructed in the Pühr area.

c. Extracting the phenols from wastes by means of a solvent have been and still are widely used for the recovery of phenol from waste liquor. A suitable solvent must be immiscible with the liquor to be treated and must easily separate from the extracted liquor, further the solubility of the phenol in the solvent must be higher than that in the liquor. With respect to the extracting properties the suitability of a solvent is indicated by the partition coefficient which is equal to the ratio of the solubilities of the substance in each solvent. The higher the partition coefficient, the smaller the volume of the solvent which is needed to give equal phenol concentrations in the treated liquor. In order to be able to select suitable solvents the partition coefficient must be determined in the laboratory. During commercial operation of a dephenolization plant the partition coefficient of the employed solvent should be calculated from the obtained analytical data at set intervals.

Determination and computation of the partition coefficient is carried out as follows;

One liter phenol containing liquor is shaken with a measured volume of the extracting solvent for such a period of time that equilibrium is obtained. The phenol content of the original liquor as well as of the treated one is determined by analysis. The phenol content of the solvent can now be easily computed. From those figures the partition coefficient can be computed.

$s$  = Phenol content of the original liquor (g per liter)

$L_1$  = Employed volume of the solvent (liter)

$L_2$  = Employed volume of the original liquor (in most cases = 1 liter)

$a$  = Phenol content of the solvent (g)

$b$  = Phenol content of the extracted liquor (g per liter)

$X$  = Partition coefficient of the solvent

$y$  = " " " " water (assumed as 1)

Phenol content of the solvent:

$$a = \frac{s \times L_1 \times X}{L_1 \times X + L_2 \times y}$$

Phenol content of the extracted liquor

$$b = \frac{s \times L_2 \times y}{L_1 \times X + L_2 \times y}$$

$$\frac{a}{b} = \frac{s \times L_1 \times X \times (L_1 \times X + L_2 \times y)}{s \times L_2 \times y \times (L_1 \times X + L_2 \times y)}$$

$$\frac{a}{b} = \frac{L_1 \times X}{L_2 \times y} ; y = 1 ;$$

$$X = \frac{a \times L_2}{b \times L_1} ; L_1 \text{ mostly } = 1 ;$$

$$X = \frac{a}{b \times L_1} = \text{Partition coefficient of the solvent.}$$

Volume of the solvent of known partition coefficient to be applied if the treated liquor shall contain a desired quantity of phenol:

$$L_1 = \frac{a}{b \times X} \quad (\text{expressed in vol. solvent per vol. liquor})$$

What phenol content of the treated liquor may be expected if the liquor is treated with  $L_1$  vol. solvent (partition coefficient  $X$ ) per vol. of liquor:

$$b = \frac{s \times L_2 \times y}{L_1 \times X \div L_2 \times X} = \frac{s}{L_1 \times X \div 1}$$

Examples:

Computation of the partition coefficient:

a) Equal volumes of liquor and solvent

determined :  $s = 4$  g per liter phenol in the original liquor

" :  $b = 1$  " " " " " " " " treated liquor

computed :  $a = s - b = 4 - 1 = 3$  g phenol in the solvent

$$X = \frac{a \times L_2}{b \times L_1} = \frac{3 \times 1}{1 \times 1} = 3.0$$

b) Applied 0.5 vol. solvent per vol. liquor

determined :  $s = 4$  g per liter phenol in the original liquor

" :  $b = 1.6$  g per liter phenol in the treated liquor

computed :  $a = s - b = 4 - 1.6 = 2.4$  g phenol in the solvent

$$X = \frac{a \times L_2}{b \times L_1} = \frac{2.4 \times 1}{1.6 \times 0.5} = \frac{2.4}{0.8} = 3.0$$

Volume solvent of known partition coefficient to be applied in order to obtain a desired phenol content of the treated liquor:

desired:  $b = 1.6$  g per liter phenol in the treated water

determined:  $s = 4$  g per liter phenol in the original liquor

computed:  $a = s - b = 4 - 1.6 = 2.4$  g phenol in the applied volume solvent

known:  $X = 3$

$$L_1 = \frac{a}{b \times X} = \frac{2.4}{1.6 \times 3} = \frac{2.4}{4.8} = 0.5 \text{ vol. solvent per vol. original liquor.}$$

What phenol content of the treated liquor may be expected if the liquor is treated with  $L_1$  vol. solvent (partition coefficient  $x = 3$ ) per vol. of liquor?

$$\text{Basic equation: } b = \frac{s \times L_2 \times y}{L_1 \times X \div L_2 \times y}$$

determined:  $s = 4$  g phenol per liter original liquor

$$\begin{array}{l} \text{known} \\ \text{"} \\ \text{"} \\ \text{"} \end{array} \quad \begin{array}{l} L_2 = 1 \\ y = 1 \\ L_1 = 0.5 \\ X = 3 \end{array}$$

$$b = \frac{s}{L_1 \times X \div 1} = \frac{4}{0.5 \times 3 \div 1} = \frac{4}{1.5 \div 1} = \frac{4}{2.5} = 1.6 \text{ g per liter}$$

$$a = \frac{s \times L \times X}{L \times X \div L \times y} = \frac{4 \times 0.5 \times 3}{0.5 \times 3 \div 1 \times 1} = \frac{6}{2.5} = 2.4 \text{ g phenol in the solvent}$$

$$s = a \div b = 2.4 \div 1.6 = 4.0 \text{ g per liter phenol in the original liquor.}$$

With respect to the economy of a commercial dephenolization process a solvent with a very high partition coefficient is not always superior to an extracting agent which has a lower partition coefficient as will be explained in the following paragraph.

Commercial operation of dephenolization plants of the extraction type means a constant fight against losses of the more or less precious solvent. We must distinguish between the solvent losses which occur in the liquor extraction system and those originating from the recovery of the phenols from the solvent. Inevitable losses are those which are due to the solubility of the solvent in the aqueous solution. Besides a high partition coefficient a suitable solvent must have a very low solubility in water. However, a low solubility in distilled water does not generally indicate the actual solubility of the solvent in all types of phenol containing liquors. Practical operation of a dephenolization plant which extracted a waste liquor originating from the carbonization of brown coal by means of a special solvent showed much higher losses of the solvent than was to be expected due to the solubility of the solvent in water. Owing to the characteristic of the carbonized brown coal the liquor

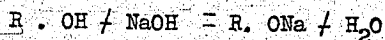


contained much more alcohols, ketones and aldehydes than usual, resulting in the fact that the solubility of the solvent in the liquor was considerably increased. The solvent losses, despite its very high partition coefficient became so high that the plant had to be shut down, whereas other plants which used the same solvent gave satisfactory results.

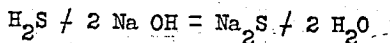
Another source of sometimes unexpected solvent losses is the formation of emulsions consisting of liquor and solvent. The emulsions floating on the surface of the liquor are carried along by the latter, resulting in losses of the solvent unless special installations are set up which recover the solvent from the emulsions. In most cases it is almost impossible to make accurate estimates with respect to the losses due to formation of emulsions from laboratory experiments because an absolutely true representative sample of the liquor to be treated is hard to obtain. Slight changes of the operating procedure of the carbonization equipment, of the condensing and oil water separating system, as well as of the type of fuels processed, may result in such a change of the properties of the liquor as to favor the formation of emulsions. Not very much is known about the type of substances which are responsible for the formation of emulsions if the liquor is free from tar oils and dust particles. Dust particles will accumulate in the interfacial layer between the solvent and the liquor, preventing a proper separation of the liquids. Since tar oils are insoluble in the liquor, they are easily extracted by the solvent raising its specific gravity, changing the surface tension at the interface between the two liquids. It is therefore necessary to liberate the liquor to be dephenolized from tar oils and dust particles. However, despite the absence of visible tar and dust particles, emulsions are sometimes formed to such an extent that the operation of the plant becomes almost impossible. I remember especially a dephenolization plant which we designed and constructed during the early days of the war. The design of the plant was a copy of at least 10 plants of the same type, the liquor

to be treated was waste liquor originating from the carbonization of coal, the coke ovens were operated at normal temperatures, the cooling system of the plant was of the standard type. Shortly after the plant had been put in operation we observed the formation of heavy emulsions which, despite all efforts, resulted in the fact that the plant had to be shut down. In this connection, I tried to find out the reason for the formation of emulsions by laboratory experiments. Equal volumes of the liquor and the solvent were poured into a graduated cylinder and stirred for a certain period of time by means of a motor driven stirrer, the speed of which could be kept constant by a rheostat. The mixed content of the cylinder was allowed to separate for 2 minutes, whereafter the interfacial layer of emulsion was read and noted. The influence of filtering, extracting, etc., on the tendency to form emulsions could so be represented by figures. The extracted organic substances were further separated by solvents and again added to distilled water in order to determine their emulsifying tendencies. The influence of dust and salts which were present in the liquor was investigated, too, as well as the influence of the p-H value of the liquor. It was so possible to trace the components which were responsible for the formation of emulsions. Since in most cases it is not possible to eliminate the emulsifying substances, provisions must be made to separate the emulsions from the liquor and to install some kind of equipment which is able to break the emulsions. In order to recover the dissolved solvent from the liquor, debenzolized gas, which easily picks up the solvent, can be passed through the liquor. By returning the saturated gas to the raw coke oven gas the solvent is recovered in the benzol scrubbers. The dephenolized liquor is transferred to the ammonia still where the ammonia together with the solvent is distilled off. By-passing the vapors through the saturator the ammonia vapors are absorbed by the sulfuric acid whereas the foul gases together with solvent vapors are returned to the crude coke oven gas.

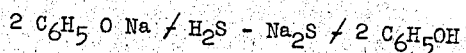
The next step is the recovery of the phenols from the solvent. There are two methods employed a chemical and a physical one. The chemical process makes react the acidic phenols with caustic soda solution forming sodium phenolate



The sodium phenolate which is insoluble in the solvent separates and can be withdrawn for further processing. It is evident that emulsions, should they be formed, represent a loss of the solvent, because in most cases the sodium phenolate solution is sold. The formation of emulsions can be prevented by operating the plant with a clean solvent. Since tar oils, should they have been present in the solvent, are insoluble in caustic soda solution, they are returned to the extracting stage and will accumulate in the solvent. In order to limit the tar oil content of the circulating liquid (formation of emulsions) part of it is branched off and distilled, whereby the tar oils due to their high boiling point remain as residue in the still. The higher the tar oil content of the liquor the larger the volume of the solvent which has to be distilled. It is obvious that all efforts must be made to obtain a sodium phenolate solution, the sodium hydroxide content of which is almost completely consumed by phenols. The waste liquors, besides phenols, ammonia etc. contain hydrogen sulfide which is partly extracted by the solvent and reacts with the caustic soda solution as well.



Since 1 g  $H_2S$  consumes 2.35 g NaOH and 1 g  $C_6H_5 OH$  only 0.43 g NaOH it is evident that even small amounts of  $H_2S$  result in considerable losses of sodium hydroxide. It is therefore advisable to remove the  $H_2S$  from the solvent prior to its liberation from the phenol compounds. The solvent is therefore treated with sodium phenolate solution, whereby the following reaction takes place:



Sodium sulfide and phenol is formed by the double reaction. The phenol is instantly dissolved by the solvent and extracted by means of caustic soda solution in the following phenol recovering stage, thus eliminating losses of phenols. As soon as the phenolate is almost decomposed the sodium sulfide solution is drained and disposed of.

The second method to recover the phenols from the solvent by distillation is possible if the boiling point of the solvent differs from that of the phenol mixture. Should the boiling point of the solvent be lower than that of the phenol mixture it can be easily distilled off, whereby the phenols remain as residue in the still. In case the boiling point of the solvent is higher, the phenols are distilled off and the solvent forms the bottom product. The difference between the two distillation processes lies in the fact that the impurities remain in the recovered phenols and an almost pure solvent is returned to the extraction if the boiling point of the solvent is lower than that of the phenols, whereas a high boiling solvent which is stripped from the phenols retains most of the impurities. Since it was pointed out in the preceding paragraphs that a clean solvent is required in order to prevent excessive formation of emulsions the distillation method combined with the application of low boiling solvents seems to offer advantages. In addition, the distillation process is obviously more simple than the extraction by means of caustic soda solutions. However, distillation consumes heat energy and considering benzol (crude light oil) as extracting agent, almost one cbm solvent has to be distilled for every cbm of liquor processed. The distillation process is economical only if very cheap steam is available. However, if a solvent is applied which has a high partition coefficient, which means that only a fraction of the volume of the processed water is needed to extract the phenols, the distillation process is the best solution to recover the phenols from the solvent.

The solvent losses are due to the following facts:

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Solubility of the solvent in the liquor to be treated,

Formation of emulsions consisting of liquor and solvent,

Formation of emulsions consisting of solvent and sodium phenolate,

Solubility of the solvent in sodium phenolate,

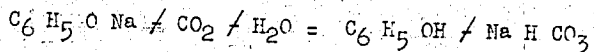
Losses due to vaporization of a low boiling solvent.

The latter are reduced if a high boiling solvent is used.

The partition coefficient has no influence on the losses of the solvent.

However, a high partition coefficient reduces the amount of energy which is needed to recirculate the solvent as well as the amount of heat energy which is required to distill the solvent.

Due to their quality the phenols which are recovered in a dephenolization plant must be refined before marketable products are obtained. At first, traces of tar oils and the solvent are removed from the phenolate by "steaming", whereafter the phenolate is "sprung" by carbon dioxide or by gases which contain high amounts of CO<sub>2</sub>.



The phenol separates as a brown oil on top of the solution of sodium salts.

It is further refined by distillation, whereby carbolic acid, o - m - p - cresol and the various xylenols are recovered. The sodium bicarbonate solution is causticized and returned to the dephenolization plant.

Since phenol (C<sub>6</sub>H<sub>5</sub>OH) is the most soluble in water of all tar acids an organic solvent will preferably remove cresols and xylenols whereas the phenol tends to remain in the liquor.

Extraction processes have been and are widely used for the recovery of phenols from waste liquors of coke oven plants, gas works, hydrogenation plants, gasification plants, brown coal processing plants, etc. A great variety of solvents has been proposed, but only a few proved successful for commercial operation.

A solvent should meet the following requirements:

1. Good solubility for phenol.
2. Low cost so that losses do not influence too much the economy of the process.
3. The solvent should be manufactured at the plant itself, so that losses can be easily replaced and that fresh solvent is always available.
4. The solvent should be almost insoluble in the liquor.
5. The solvent should have no emulsifying tendencies.
6. The solvent should not be decomposed by alkali or during the distillation process.
7. The solvent should have a low vapor pressure.
8. The specific gravity of the solvent should differ sufficiently from that of the liquor, so that separation by gravity takes place.
9. The phenol should be easily recoverable from the solvent.

Experience shows that probably no solvent can satisfy all requirements.

The mostly used benzene (light oil) or certain oil fractions are comparatively cheap and are manufactured at the plant itself, but the partition coefficient is low, requiring large quantities of the solvent to be recirculated and processed. Synthetic solvents such as "Phenosolvan" and "Tricresyl phosphate" have a high partition coefficient, however, are comparatively expensive and must be purchased from outside sources. Hence, losses, which can never be eliminated, influence seriously the economy of the process.

The following methods or solvents were used in Germany for the extraction of waste liquors:

Coke oven plants, gasworks: benzene extraction.

Hydrogenation plants: tricresyl phosphate extraction; extraction by means of middle oil originating from the hydrogenation of coal.

Brown coal processing plants: tricresyl phosphate extraction; phenosolvan  
Extraction; Koppers vapor recirculation  
process; middle oil from brown coal carbon-  
ization (in experimental stage).

### Benzene extraction

Benzene or, to be more correct, crude light oil, which originates from the carbonization of coal and has been extracted from the coal gas by scrubbing the latter with wash oil, has been almost exclusively used for processing waste liquors of coke oven plants and gas works. Its partition coefficient is rather low so that 0.9 - 1.2 volumes of solvent per volume of liquor have to be employed in order to obtain a 90% dephenolization of the liquor. However, the solvent is cheap and since light oil is continuously produced by the carbonization of coal, losses can be easily replaced. In 1939, there existed 28 plants which extracted the phenol from waste liquor by means of benzene. Since steam was rather expensive the extracted phenol was mostly recovered from the benzene by means of caustic soda solution. Some of the plants were equipped with an installation which recovered the benzene from the extracted liquor and which proved very satisfactory. With the exception of one plant the formation of emulsions could be kept within reasonable limits. The last traces of tar oils were removed from the liquor by a separate wash with crude light oil, which was occasionally liberated from the absorbed tar oils by distillation. Since the partition coefficient increases with a rising temperature, provisions were made in order to be able to preheat the liquor to 40 - 50°C. Prior to the removal of the phenol from the solvent by means of caustic soda solution dissolved H<sub>2</sub>S was absorbed by sodium phenolate solution. Part of the recirculated solvent was branched off and liberated from simultaneously absorbed tar oils by distillation.

Some operating data from a 6 days test run were as follows:

Throughput of crude liquor:	453 cbm per 24 hours	
Recirculated benzene:	398 " " " "	= 0.88 vol. solvent per vol. of treated liquor
Fresh water for cooling purposes	201 " " " "	= 0.45 cbm per cbm liquor
Steam for preheating the liquor and distilling part of the solvent	14,116 kg per 24 hours	= 31 kg per cbm liquor

The dephenolization effect was 85 - 90%.

In order to be able to reduce the size of the absorber, very slowly rotating perforated paddles were arranged between the usually employed sieve plates. Liquor and light oil are continuously passed through the absorber in counter current flow, whereby the liquor is admitted in the top of the tower and the light oil in the bottom, the liquids are withdrawn by means of adjustable seals.

When continuing the description of processes which utilize low boiling solvents the "Phenosolvan - process" must be mentioned. Phenosolvan is a solvent consisting of esters of carboxylic acids such as ethyl acetate and butyl acetate (ethyl acetate,  $\text{CH}_3 \cdot \text{COO} \text{C}_2 \text{H}_5$ , density 0.901, boiling point  $77.15^\circ\text{C}$ , butyl acetate  $\text{CH}_3\text{COO} \cdot (\text{CH}_2)_3 - \text{CH}_3$ , density 0.882, boiling point  $126.5^\circ\text{C}$ ). The absorbed phenol can now be recovered from the solvent by distillation, thus providing the extraction system with an almost pure solvent which in turn eliminates the formation of emulsions. The low density of the solvent allows the extracted liquor to separate by gravity in a relatively short period of time. Not very much experience from practical operation of commercial plants is available. However, the results which have been obtained from the operation of pilot plants were so encouraging that it was contemplated to apply the



Phenosolvan process for processing the waste liquors which were expected to originate from low temperature carbonization of coal. A middle oil which was distilled from coal tar was used for the dephenolization of waste liquors of coke oven plants too. The phenol was recovered by caustic soda from the spent oil. However, it was experienced that the light oil which originates from high temperature carbonization of coal was more convenient to handle resulting in the fact that waste liquors of coke oven plants were almost entirely treated with light oil.

Large volumes of phenol containing waste liquors are produced by the hydrogenation process of coal. With the growing accumulation of the industry in the Ruhr area as well as in Middle Germany provisions had to be made in order not to pollute the streams. In the brown coal district of Middle Germany the "Tricresyl phosphate process" was used which will be described in one of the following paragraphs.

However, it was found out that middle oils originating from the hydrogenation of coal were satisfactory solvents for the phenols. Due to a content of tar bases the oils had a fairly good partition coefficient. Since the tar bases are soluble in water they are slowly extracted during the dephenolization process, thus lowering the efficiency of the extraction. It was therefore contemplated to replace the oil in short intervals, which could be easily done, because sufficient middle oil was continuously produced. The middle oil was merely an agent which was passed through the dephenolization system before being further processed. A commercial plant was put in operation near the end of the war. The utilization of hydrogenation middle oil was another step to use solvents which were produced at the plant itself in order to become independent from chemicals which had to be purchased.

Waste liquors originating from the low temperature carbonization of brown coal contain large amounts of phenol which had to be extracted. Many experiments have been carried out in order to utilize the light oil scrubbed from the

brown coal gas. However, due to the paraffinic character of the light oil the partition coefficient was too low as to guarantee a satisfactory extraction applying reasonable volumes of the recirculating agent. In addition, the light oil became almost ineffective after a short period of time. Hunting for a more efficient solvent I. G. Farben developed the Tricresyl phosphate process. Since the Dr. C. Otto Company acquired an exclusive license for the design and construction of commercial plants of this type, I had the opportunity to watch the development of the process from the very beginning.

Tri-o-cresyl phosphate ( $(\text{CH}_3 \text{C}_6\text{H}_4)_3 \text{PO}_4$ ) is a liquid which before boiling at normal pressure begins to decompose at  $410^\circ\text{C}$ . Under an absolute pressure of 20 mm Hg it boils between  $263 - 265^\circ\text{C}$ . The density is about 1.18 and the molecular weight as high as 368.36. Unlike the already mentioned solvents, the density is higher than that of the waste liquor to be treated and the boiling point is higher than that of the phenol.

The partition coefficient is much higher than that of light oil originating from coal carbonization as shown by the following table:

	Partition coefficient with		
	Tricresyl Phosphate	Benzol	Ratio of Partition Coefficients
Phenol	60	1.9	31
O - Cresol	210	13.0	16
p - Cresol	196	11.5	17
Phenol mixture in waste liquor	88	5.2	17

Due to the high partition coefficient the volume to be applied was only 8 - 10% of the volume of the liquor to be processed. Three comparatively small vessels which were connected in series were passed by the solvent and the liquor in a counter current flow. An intimate contact of the liquids was secured by slowly rotating paddles. Due to the high density of the solvent it was drained

from the cone shaped bottom of the vessel whereas the processed waste liquor was passed through a following separating vessel packed with Raschig rings in order to remove the last traces of the solvent. The tiny solvent particles should be retained by the Raschig rings and assembled to larger drops which were expected to separate more easily from the waste liquor. Due to the very low solubility of the solvent in water the solvent losses were supposed to be extremely low which in turn was necessary because the solvent was very expensive. What sometimes actually happened with respect to the losses shall be mentioned in one of the following paragraphs.

The phenol cannot be extracted from the solvent by means of an alkali owing to heavy emulsions which are formed. Separation by distillation was therefore employed. Since the boiling point of the phenol is lower than that of the solvent, the phenol is distilled off from the latter. However, in order to keep the distillation temperatures as low as possible a high vacuum was applied. The first commercial plant was equipped with a still and condenser standing high above the ground, the condensate carrying tube was led to the ground floor of the plant thus creating a natural vacuum. However, in order to save height, the following plants were equipped with a vacuum pump which sucked the vapors from the still.

The distilling column was packed with Raschig rings and equipped with a separator which retained the solvent mist entrained in the vapors. The difference of the boiling points between those of the phenol and the solvent was large enough as to prevent losses of the solvent due to its vapor pressure. With the phenol being the lower boiling component it is obvious that high boiling tar oils accumulate in the solvent increasing its viscosity and tendency to form emulsions.

Since separation by distillation was not possible, a chemical treatment had to be applied. The basic idea of the refining procedure was as follows: The tar oils which were present in the solvent were polymerized by concentrated sulfuric acid (oleum), whereafter the asphaltic substances were absorbed by pulverized limestone and separated from the solvent by means of a centrifuge. It is evident that such a procedure was a nuisance, the operator was molested by the acid fumes, sometimes the more or less viscous mixture was spilled when the pulverized limestone was admixed owing to a rapid  $\text{CO}_2$  - evolution. Considerable amounts of solvent were absorbed by the limestone - asphalt mixture which was removed from the centrifuge. Despite all assurance that the oleum would not attack the solvent we investigated the refining procedure carefully in the laboratory. It was found out that the oleum attacked the tricresyl phosphate forming mono - and di - cresyl phosphate ( $(\text{CH}_3\text{C}_6\text{H}_5)_2\text{HPO}_4$  and  $(\text{CH}_3\text{C}_6\text{H}_5)_2\text{HPO}_4$ ). While the solubility in water of the tricresyl phosphate is very low, the mono - and di - cresyl phosphate shows a much higher solubility resulting in the fact that the refined solvent is more easily dissolved by the liquor, thus increasing the inevitable losses. It is evident that a solvent which has to extract a waste liquor which contains larger quantities of tar oils must be more frequently refined, thus increasing the solvent losses. As a result of our investigations I. G. Farben replaced the sulfuric acid by phosphorus acid which was supposed not to attack the tricresyl phosphate. I tried to find a selective solvent which extracts either the asphaltic substances and does not touch the tricresylphosphate or dissolves the tricresylphosphate, whereas the asphalts are precipitated. It was found out that benzine or paraffinic oils of a somewhat higher boiling point would dissolve the tricresylphosphate at elevated temperature, leaving the asphaltic substances untouched so that they were able to be separated by filtering or centrifuging. Cooling,

the solution results in a fairly good separation of the benzine from the tricresyl-phosphate because the latter becomes almost insoluble in cold benzine. The rest of the tricresyl-phosphate can be recovered by vaporizing the benzine or the already saturated benzine is used for the following refining procedure. A semi-commercial experiment was carried out and proved very satisfactory.

A commercially sized pilot plant was operated at the Leuna Factory which showed satisfactory results with respect to the extraction and the losses. Later on we designed and constructed a dephenolization plant for the Hefrag near Frankfort (Main). The plant was supposed to process waste liquor originating from low temperature carbonization of brown coal. The phenol was fairly well extracted, but considerable losses of the solvent were observed. The waste liquor contained occasionally oil and tar resulting in the formation of emulsions, which floated on the surface of the treated liquor and were not separated during the passage through the Raschig ring packed separator. The viscous emulsions were deposited on the surface of the rings blocking the proper flow of the liquor. The packing had to be removed at short intervals and be cleaned by caustic soda solutions. We practiced various methods to separate the tar particles from the liquor prior to its admission in the extracting vessels. Finally it was found out that a layer of piassava brooms was able to retain the oil and tar particles. But even with a properly cleaned water the solvent losses were much too high. One reason for the losses was the frequent treatment of the solvent with concentrated sulfuric acid, whereby water soluble substances were formed as mentioned before. Exhaustive investigations of the waste liquor showed that considerable amounts of ketones, aldehydes, higher boiling alcohols, etc., were present in the waste liquor, which increased the solubility of the solvent in the wastes. There was no way to remove these objectionable substances at reasonable cost. It was contemplated

to produce phenol, cresol, etc., from the extracted phenol mixture. However, it was experienced that the fractions which were obtained by distillation did not meet the specifications. Numerous analyses showed that the phenol mixture was accompanied by fatty acids which had the same boiling range as the phenol, thus preventing a proper separation by a distillation process without a preceding chemical treatment. Although nobody expected to make any profits from the phenol extraction, the losses were so high that we were forced to shut down the plant and to refund the Hefrag. The excessive losses were not solely due to a failure of the process, the abnormal composition of the waste liquor to be treated was equally responsible. At least 5 more plants of this type were constructed, which were operated more successfully although the solvent losses were sometimes higher than expected. Three plants had to process waste liquor originating from the hydrogenation of brown coal or brown coal tar which offered less difficulties than those which extracted waste liquor from the carbonization of brown coal. It is obvious that the reputation of the tricresyl phosphate process was not too good and that the brown coal processing companies were greatly interested to use a more economical process.

In order to become independent from the purchase of a more or less expensive solvent, it was again tried to use a solvent which originates from the carbonization of brown coal itself. Light oil was not suitable as pointed out before. However, it was found that middle or fuel oil fractions of brown coal tar, the phenol content of which had been previously extracted, gave satisfactory results. The partition coefficient was as high as that of coke oven light oil and no rapid decrease of the absorption efficiency was observed. Since fuel oil is continuously produced by the carbonization process, the oil can be easily replaced after a short period of operation.

A pilot plant was successfully operated with waste liquor and a fuel oil fraction. The plant consisted of a combination of mixing pumps and centrifuges, thus eliminating absorbers and separating vessels. The fuel oil was passed in a counter current flow to the waste liquor through the pumps and centrifuges connected in series. The phenol was extracted from the fuel oil by means of caustic soda using a mixing pump centrifuge system too. Each mixing pump was followed by a centrifuge which separated the two liquids which were then passed to the following mixing pump, etc. The best results were obtained when both waste liquor and solvent originated from the carbonization of the same coal.

d) The extraction of phenols from waste liquors by means of solvents is connected with inevitable losses of the solvent. For economical reasons the solvent losses should be kept at a minimum. Although a solvent which has a high partition coefficient offers many advantages, its applicability is doubtful; if due to excessive losses of an expensive solvent, the process becomes uneconomical. It is therefore obvious that great efforts have been made to recover the phenol from waste liquors without using a solvent.

Since phenol has a fairly high vapor pressure particularly at steam temperatures, experiments were carried out to remove the phenol from the waste liquor by means of cheap fuels whereby the phenol is supposed to be completely vaporized after a small percentage of the liquor has been distilled. The condensate was redistilled until the phenol was concentrated to such an extent that it separated from the water. However, it was found that an appreciable volume of the crude liquor had to be vaporized in order to obtain a 90% dephenolization effect. The fuel consumption would be very high in order to carry out the various distillation steps.

The Koppers vapor recirculation process was the first solution of the problem to eliminate the utilization of a solvent which was commercially

employed. A current of steam is continuously recirculated through the waste liquor in order to vaporize the phenol, and afterwards through a hot caustic soda solution to separate the phenol from the steam. The dephenolization effect is very good; however, due to the high temperature of the caustic soda solution the available caustic could not be totally converted to sodium phenolate. In order to make full use of the caustic, the diluted sodium phenolate solution was applied to extract phenol from light oil or other phenol containing oils. The process was employed, too, for the dephenolization of waste liquors originating from the carbonization of brown coal. I have tried to point out that the dephenolization of waste liquors, similar to the desulphurization of gases, requires much experience and skill not only in the design but in the operation of the plants, also.

B. Determination of the partition coefficients of the constituents of a brown coal fuel oil, influence of admixtures on the partition coefficient, influence of the content of free ammonia of the waste liquor on the phenol extraction.

In one of the preceding paragraphs experiments were described which used brown coal middle or fuel oil for the extraction of phenol from waste liquor. The fuel oil showed a fairly high partition coefficient. In this connection it was of interest to determine the extracting efficiency of the various constituents of the employed oil. Since it was impossible to separate the single components, another procedure had to be employed in order to obtain a rough estimate of the efficiency of the constituents. At first the partition coefficient of the original oil and that of the oil the phenol of which had been extracted was determined. Subsequently the tar bases were extracted by means of diluted sulfuric acid and the partition coefficient was determined again.



A following extensive treatment with 85% sulfuric acid removed the unsaturated hydrocarbons. The solvent consisted then of aromatic and saturated aliphatic hydrocarbons. Finally the aromatic hydrocarbons were extracted by means of 96% sulfuric acid, leaving an oil which contained mostly saturated aliphatic hydrocarbons. By the application of this procedure it was now possible to determine the extracting efficiency of the various components of the brown coal fuel oil with respect to aqueous solutions of phenol, cresol and xylenol and a waste liquor of brown coal gasifying producers.

Table 1 represents the properties of the brown coal oil during the course of the separating procedure.

TABLE 1  
Properties of the Brown Coal Oil during the Course of the Separating Procedure

Stage of the procedure	1	2	3	4
Extracting agent	none	caustic soda	oil H <sub>2</sub> SO <sub>4</sub>	85% H <sub>2</sub> SO <sub>4</sub>
Extracted components	none	phenol	tar bases	unsat. aromatic hydroc.
Retained components	phenol tar bases unsat. aromat. sat. aliph. hydroc.	phenol tar bases unsat. aromat. sat. aliph. hydroc.	tar bases unsat. aromat. sat. aliph. hydroc.	aromat. sat. aliph. hydroc.
Boiling analysis of the oils	174	180	185	186
% vol.	2.5	1.0	1.0	1.5
" "	5.0	2.0	2.0	2.5
" "	8.5	4.0	4.0	3.5
" "	12.5	4.0	8.0	5.5
" "	16.5	10.0	12.5	8.0
" "	22.5	17.5	17.0	13.0
" "	29.5	20.0	22.0	16.0
" "	36.0	27.5	30.0	24.0
" "	43.0	40.0	38.0	58.0
" "	51.5	45.0	44.0	35.0
" "	59.5	53.5	51.0	41.0
" "	64.5	58.0	56.0	49.0
" "	70.0	65.0	65.0	56.0
" "	74.5	71.0	71.0	58.5
" "	79.0	76.5	76.5	64.5
" "	83.0	79.5	80.0	67.5
" "	86.0	84.0	84.0	70.0
" "	91.0	87.5	87.0	74.5
" "	0.9008	0.9000	0.9000	0.9040
Spec. grav. 20°C	195	193	197	226
Mol. wt				
				190
				0.5
				1.0
				4.5
				7.5
				10.5
				14.0
				18.0
				23.0
				27.0
				35.0
				40.0
				43.0
				48.0
				53.0
				57.0
				62.0
				68.0
				0.6766
				246

The boiling analysis of the various oils is subject to slight changes. The specific gravity is almost equal; however, after the removal of the aromatic hydrocarbons it declines sharply. The molecular weight increases slowly with an increasing amount of paraffinic hydrocarbons.

The following Table 2 represents the partition coefficients for phenols between the oils 2-5 and water

Tar acid	Phenol	o - cresol	m - cresol	p - cresol
concentration mg per liter	5,230	5,180	4,950	4,250
partition coefficient of oil 2	2.8	2.8	7.6	6.2
" " " 3	2.8	3.0	7.0	6.5
" " " 4	0.8	0.6	1.2	1.5
" " " 5	0.6	0.4	0.6	0.5
Tar acid	1,2,4 -xylenol		1,3,4 -xylenol	1,3,5 -xylenol
concentration mg per liter	1,010		3,530	3,370
partition coefficient of oil 2	6.2		22.5	16.3
" " " 3	10.1		26.2	21.8
" " " 4	2.7		10.4	4.2
" " " 5	0.3		2.5	2.0
Tar acid	1,4,5 -xylenol			waste liquor from producer
concentration mg per liter	2,520			11,750
partition coefficient of oil 2	24.6			5.1
" " " 3	24.7			5.1
" " " 4	4.2			3.0
" " " 5	1.7			1.7

The removal of the comparatively small amounts of tar bases influences the partition coefficient very little. However, the latter drops sharply when the unsaturated hydrocarbons have been extracted, thus indicating that the unsaturated hydrocarbons, which are present in the brown coal fuel oil, are very efficient with respect to the extraction of phenol from water.

Another decline of the partition coefficient was observed when the aromatic hydrocarbons had been removed by means of 96% sulfuric acid from which it is concluded that aromatic hydrocarbons have a good extraction efficiency, too. Unsaturated and aromatic hydrocarbons seem to be the active agents which are responsible for the extracting efficiency of the brown coal fuel oil. A better comparison of the influence of the various hydrocarbon classes on the partition coefficient is offered by expressing the determined values as per cent of the partition coefficient of the phenol free oil, whereby the latter is marked with 100.

Table 3

Tar acids	phenol	cresol	xylenol	phenol mixture
phenol free oil	100	100	100	100
unsaturated hydrocarbons extracted, oil cont. aromatic and sat. aliph. hydrocarbons	28.6	34.5	33.2	58.8
Aromatic hydrocarbons extracted, oil cont. sat. aliphatic hydrocarbons	21.4	10.1	8.8	33.4

The extracting power is reduced to about  $1/3$  of the original value when the unsaturated hydrocarbons have been extracted, and another sharp decline is followed by the removal of the aromatic hydrocarbons.

It is evident that the partition coefficient of a solvent can be raised by the admixture of tar bases, because the physical extraction is aided by an additional chemical reaction. In order to determine the suitability of various tar bases, the effect of a 5% admixture on the partition coefficient was investigated.

The following tar bases were admixed:

pyridine  $C_5H_5N$

Aniline  $C_6H_5NH_2$

O - toluidine  $CH_3C_6H_4NH_2$

dimethyl toluidine  $CH_3C_6H_4N(CH_3)_2$

dimethyl aniline  $C_6H_5N(CH_3)_2$

quinoline  $C_9H_7N$

The following table 4 contains the results of the experiments:

TABLE 4

Effect of an admixture of tar bases on the partition coefficient

Tar acids concentration mg per liter	waste liquor	phenol	o-cresol	m-cresol	p-cresol	1,2,4-xyleneol	1,3,4-xyleneol	1,3,5-xyleneol	1,4,5-xyleneol
11,570	5,230	5,180	4,950	4,250	1,010	3,530	3,370	2,520	
oil free from phenols and bases	5.1	2.8	2.8	7.6	6.2	6.2	22.5	16.3	24.6
admixture of 5% pyridine	26.3	7.7	7.4	15.0	17.1	20.1	31.3	27.1	20.0
quinoline	24.5	15.9	13.8	21.0	22.6	19.4	15.8	18.2	12.2
aniline	7.8	4.0	3.9	5.1	7.3	11.7	19.8	15.4	21.1
dimethyl aniline	7.3	2.1	2.9	8.2	6.7	15.9	21.1	20.1	15.8
O-toluidine	5.0	3.5	0.9	1.7	1.1	0.9	1.5	7.9	1.6
dimethyl toluidine	6.7	3.2	3.1	8.2	2.8	16.6	16.7	20.1	17.7

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A considerable increase of the value of the partition coefficient can be obtained only by an admixture of pyridine or quinoline. Other tar bases produce almost no effect.

Since it may be of interest to raise the partition coefficient of a solvent, some experiments were made with the scope to determine the necessary amount of tar bases which is required to improve the efficiency of the brown coal oil. Owing to the good results which had been obtained by admixing pyridine or quinoline, the influence of an admixture of those two bases was investigated. Aqueous solutions of phenol and p-cresol were treated with the already employed brown coal oil which was blended with increasing volumes of pyridine or quinoline. The results are represented by the attached diagram 1. With an increasing admixture of bases the slope of the curve is very steep at first. However, it becomes more and more straight with a still higher volume of bases added. The flattening of the curve begins with an admixture of 3 - 6 mole bases to the oil per 1 mol phenol in the liquor to be treated. By admixing 1 - 2% of the bases to the oil the partition coefficient can be almost doubled with respect to the extraction of phenol. It is now possible to extract a higher percentage of phenol than usual. Since the bases are more or less soluble in water, the losses should be made up by a continuous admixture of bases in order to maintain the efficiency of the solvent.

Most of the liquors to be dephenolized do not contain the phenol in an aqueous solution but in a diluted solution of ammonia in water. While the presence of tar bases in the solvent improves its effect, an ammonia content of the liquor should exercise a deleterious effect on the phenol extraction. The acidic phenols are neutralized by bases under the formation of salts. Phenols cannot be extracted from salts by solvents, unless the salts are

decomposed by hydrolysis or dissociation. With an increasing amount of free ammonia the dissociation of the ammonium phenolate will be retarded, resulting in a decrease of the apparent partition coefficient.

In order to obtain figures representing the dependence of the apparent partition coefficient upon the presence of various amounts of free ammonia, numerous experiments were carried out. Brown coal fuel oil liberated from phenol and bases was used as solvent for the extraction of phenol and cresol from aqueous solutions.

The results are represented by the following tables:

a) concentration of the solution:  $4.47 \text{ g per liter} = 0.048 \text{ mole per liter phenol}$

Ammonia concentration of the solution		phenol content after the extraction		% extracted	partition coefficient
g/l	mole/l	mole $\text{NH}_3$ per mole phenol	g/l		
0.0	0.0	0.0	1.60	64.3	1.79
0.05	0.003	0.06	1.43	68.0	2.13
0.10	0.006	0.12	1.55	65.5	1.88
0.18	0.011	0.21	1.63	63.6	1.74
0.25	0.015	0.31	1.74	61.1	1.57
0.51	0.030	0.62	1.92	57.1	1.33
0.95	0.056	1.17	2.05	54.2	1.18
3.0	0.177	3.69	2.65	40.8	0.69
4.96	0.292	6.08	2.94	34.3	0.52
10.00	0.589	12.28	3.25	27.6	0.38
18.90	1.11	23.10	3.67	17.9	0.22
46.0	2.71	56.50	4.05	9.4	0.10
80.0	4.71	98.20	4.06	9.2	0.10



b) concentration of the solution: 5.40 g per liter - 0.05 mole per liter p - cresol

Ammonia concentration of the solution		cresol content after the extraction		% extracted	partition coefficient
g/liter	mole/liter	mole NH <sub>3</sub> per mole p-cresol	g/liter		
0.0	0.0	0.0	0.88	83.6	4.89
0.41	0.024	0.48	1.02	81.0	4.29
0.61	0.036	0.72	1.25	78.6	3.32
1.0	0.059	1.18	1.27	76.5	3.33
3.0	0.177	3.54	1.51	72.0	2.58
5.0	0.294	5.88	1.91	64.5	1.83
9.86	0.580	11.62	2.11	60.9	1.56
30.0	1.77	35.4	2.65	50.9	1.04

Diagram II represents the results of the experiments.

The figures and the curves show very clearly that with an increasing content of free ammonia in the liquor the partition coefficient and the extractor power of the solvent are decreasing. It becomes more and more difficult to obtain a low phenol content in the treated liquor unless larger volumes of solvent are used.

The curves indicate, that already small amounts of free ammonia exercise a deleterious effect on the partition coefficient of the solvent. However, the influence becomes less important, when the content of free ammonia exceeds 10 - 20 moles ammonia per mole tar acid. Such a decrease of the partition coefficient will not be too important if waste liquor originating from low or high temperature carbonization of coal has to be extracted because most of the ammonia is combined with carbon dioxide and hydrogen sulfide. However, the influence becomes apparent if concentrated ammonia liquors which are almost free from CO<sub>2</sub> and H<sub>2</sub>S have to be dephenolized.

Summary; Experiments have shown that the good extraction effect of a brown coal fuel oil depends on the presence of unsaturated and aromatic hydrocarbons. The partition coefficient of a solvent can be raised by admixing tar bases. The presence of free ammonia in the liquor to be extracted exercises a deleterious effect on the efficiency of the applied solvent.

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EFFECT OF THE ADMIXTURE OF TAR BASES ON THE PARTITION COEFFICIENT

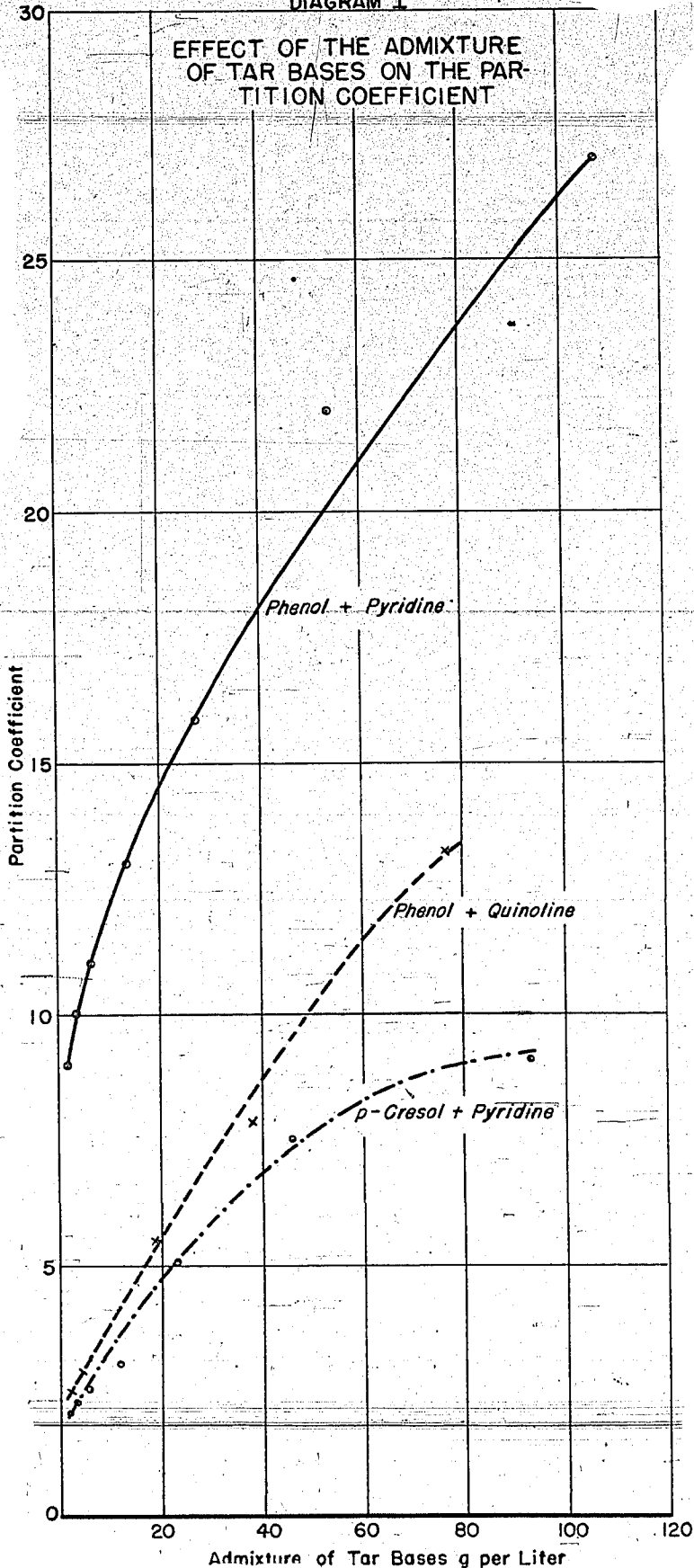


DIAGRAM II

