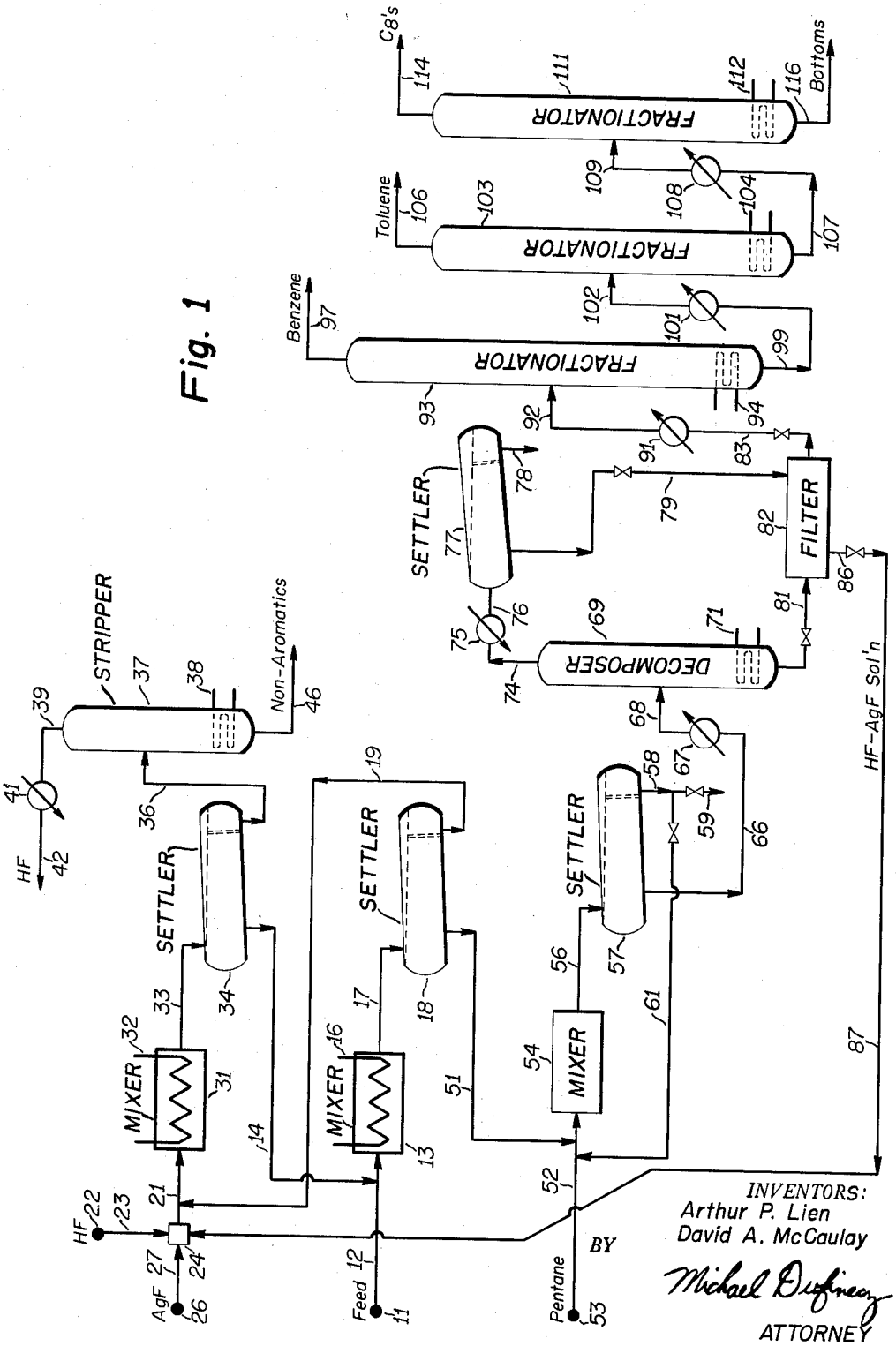
July 19, 1955 A. P. LIEN ET AL 2,713,552

EXTRACTION OF AROMATICS FROM NAPHTHAS

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Fig. 1



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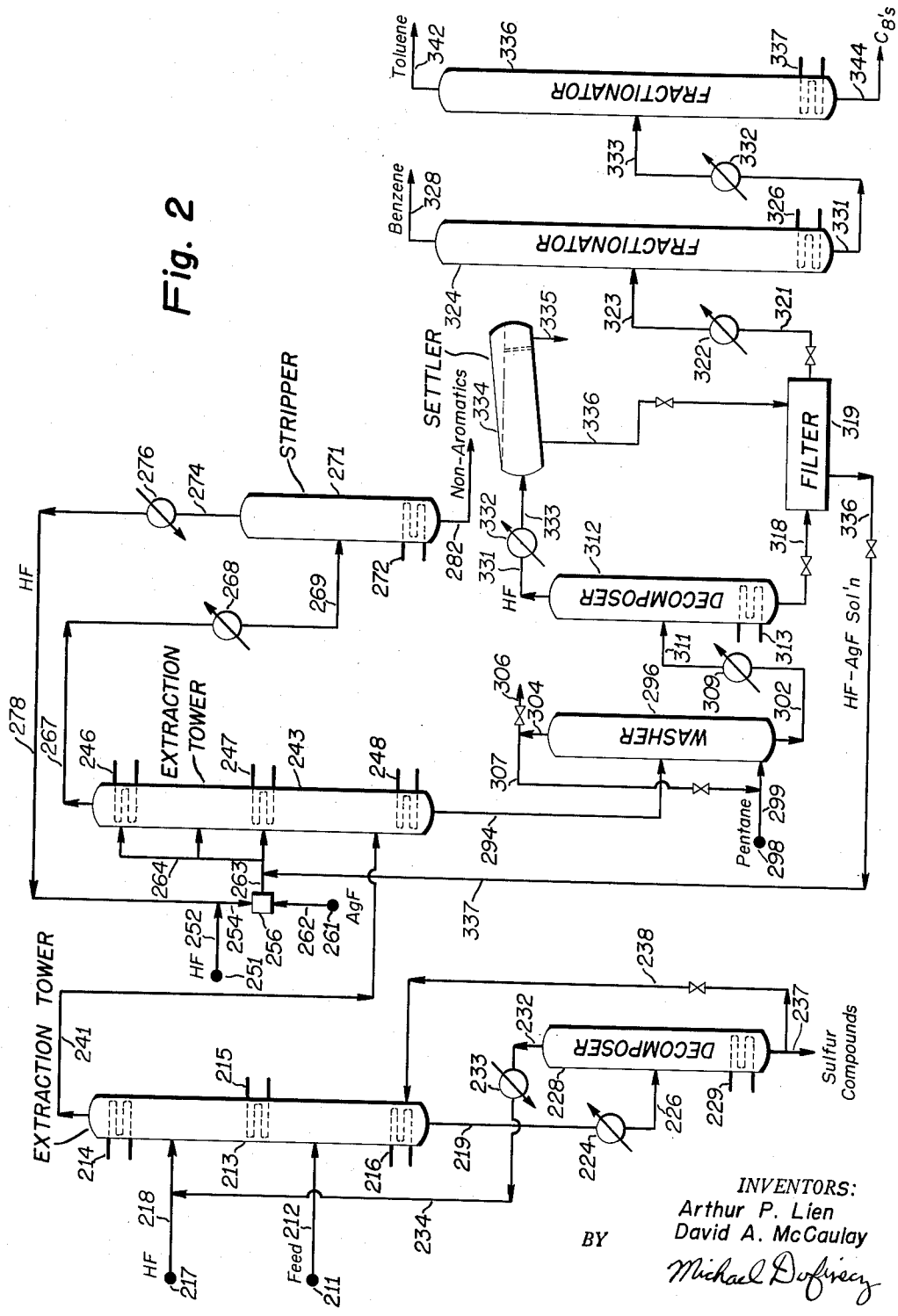
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EXTRACTION OF AROMATICS FROM NAPHTHAS

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Fig. 2



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EXTRACTION OF AROMATICS FROM NAPHTHAS

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Application October 17, 1951, Serial No. 251,692

5 Claims. (Cl. 196—13)

This invention relates to the recovery of aromatic hydrocarbons from a mixture of hydrocarbons boiling in the naphtha range, i. e. below about 450° F. and preferably below about 325° F. More particularly, the invention relates to the recovery of benzene, toluene, ethylbenzene and xylenes from petroleum naphthas containing these aromatics.

Aromatic hydrocarbons exist in virtually all crude oils. The separation by fractional distillation of these aromatics from the non-aromatics, i. e. paraffins, naphthenes, organic sulfur compounds and—in the case of naphthas derived from thermal or catalytic cracking operations—olefins and oxygenated compounds such as alkylphenols, is extremely difficult because members of the various classes of hydrocarbons have similar boiling points. The solvent extraction processes for improving the quality of lubricating oil fractions are not suitable for the recovery of aromatics boiling in the naphtha range. While liquid SO_2 extraction has been adapted to benzene and toluene recovery, it suffers from the disabilities of operating at rather low temperature and relatively low percentage recovery. Now in commercial use are processes using extractive distillation or azeotropic distillation for the recovery of the aromatic hydrocarbons boiling in the naphtha boiling range, i. e. benzene, toluene, ethylbenzene and the xylenes. These processes all possess certain disabilities ranging from low percentage recovery to an inability to recover more than one substantially pure aromatic constituent in a given integrated process.

It is an object of our invention to recover the aromatic constituents from aromatic-containing hydrocarbon mixtures boiling below about 450° F. Another object of our invention is to treat an aromatic-containing naphtha boiling below about 325° F. in order to obtain the aromatic constituents thereof substantially free of interfering non-aromatics so that individual aromatic compounds may be separated by simple fractional distillation. A further object of our invention is to develop a process for the recovery of aromatics, such as benzene, toluene, mixed xylenes and ethylbenzene from petroleum naphthas by extraction thereof with a treating agent consisting of silver fluoride dissolved in liquid hydrogen fluoride.

In our previous work on the treatment of aromatic hydrocarbons with BF_3 dissolved in liquid HF, we found that BF_3 forms a complex with polyalkyl aromatic compounds, which complex is very soluble in liquid HF. However, benzene and toluene do not form complexes with BF_3 and so cannot be separated from admixture with non-aromatic compounds, except to the extent of their slight solubility in liquid HF. Contrary to our experience with BF_3, we have discovered that silver fluoride in the presence of liquid HF will react with benzene, toluene, ethylbenzene and other alkylbenzenes in addition to the polyalkyl benzenes and polynuclear aromatics to form a complex, which complex is very

soluble in liquid HF. Furthermore, unlike BF_3, AgF has no catalytic effect, insofar as disproportionation or isomerization reactions are concerned, upon aromatics present in liquid HF in the form of an AgF-aromatic complex.

The solubility of benzene and toluene in liquid HF at about 70° F. is about 3 volume percent and the solubility of xylene is about 2 volume percent. We have found that more aromatic hydrocarbon can be taken up by liquid HF when silver fluoride is dissolved therein than is capable of going into solution in liquid HF alone. This increase in solubility is due to the formation of a complex consisting of aromatic hydrocarbon, AgF and (we believe) HF. This complex is extremely soluble in liquid HF; it is possible to have more AgF present in a complex-liquid HF solution than liquid HF alone is capable of dissolving. This complex is stable in the presence of liquid HF at ambient temperatures. The components of the complex can be recovered readily by distilling away the HF and aromatic hydrocarbon whereupon the AgF remains behind in the vessel in the form of a very finely divided solid. Within the limits of possible experimental error we have found that 1 mol of AgF and 3 mols of aromatic hydrocarbon such as benzene, toluene, xylene or ethylbenzene are present in each mol of complex; we believe that HF is a necessary constituent of the complex because no complex is formed in the absence of HF, but we do not know just how much HF is contained therein.

Silver fluoride is a crystalline solid with a melting point of 815° F. It is very soluble in liquid HF and passes into solution readily. The solubility at about 0° F. is 33 grams per 100 grams of HF or 0.26 mol of AgF per 100 ml. of liquid HF. The AgF may be recovered from its solution with liquid HF by distilling off the HF.

We have found that when a mixture of aromatic hydrocarbons—such as benzene, toluene, xylene and ethylbenzene—and non-aromatic hydrocarbons is treated with a solution of AgF in liquid HF, an upper raffinate phase and a lower extract phase is obtained. The upper raffinate phase consists of a very small amount of liquid HF and a mixture of hydrocarbons, which mixture contains a smaller percentage of aromatics than the feed mixture. The extract phase consists of liquid HF, complex, and physically dissolved aromatic and non-aromatic hydrocarbons; the extracted hydrocarbons recovered from the liquid HF-AgF treating agent consist predominantly of aromatics—usually the extracted hydrocarbons will contain substantially less than 20% of non-aromatic hydrocarbons.

The percentage recovery, in a single contacting stage, of the aromatic hydrocarbons present in the feed mixture is dependent upon the amount of AgF present in the treating agent. We have found that 70 to 75 volume percent of the aromatics in the feed can be readily extracted by using 1 mol of AgF for each 3 mols of aromatics to be recovered. To our surprise we have discovered that the use of the theoretical amount of 1 mol of AgF for each 3 mols of aromatic in the feed mixture will not remove more than 80 to 85% of the total aromatics therein, in a single contacting stage. For example, with a feed mixture containing about 40% of xylenes, about 85% of the xylenes can be extracted by using 0.4 mol of AgF per mol of xylene in the feed. By using 1 mol of AgF per mol of xylene, it is possible to extract essentially all the xylenes from the feed in a single contacting stage. It is somewhat more difficult to extract benzene and toluene from admixture with non-aromatic hydrocarbons of about the same boiling point. In order to recover about 85% of the benzene contained in a feed consisting of 40% benzene and 60%

non-aromatic, it is necessary to use at least about 0.5 mol of AgF per mol of benzene in the feed. By using at least about 0.8 mol of AgF per mol of benzene, as much as 95% of the benzene can be recovered in a single stage.

Some gain in extraction efficiency can be obtained by using countercurrent multi-stage contacting, either batch multi-stage or continuous tower operation; however, normally a single contacting stage with adequate mixing will produce results almost as good as multi-stage contacting. In the case of single-stage contacting, more AgF based on aromatics present in the feed stock is required. Thus for the recovery of 70 to 75% of the aromatics present in mixed hydrocarbons boiling below 450° F. and preferably below about 325° F., we use one-third mol of AgF for each mol of aromatic that it is desired to extract from the feed mixture. In order to recover more than 70 to 75%, it is necessary to use at least about one-third mol of AgF per mol of aromatic present in said feed. While the amount of AgF needed per mol of aromatic present in a mixed hydrocarbon feed will vary somewhat with the type and amount of aromatic present in said feed, it is possible to recover in excess of 80% of said aromatics in a single contacting stage by using at least about 0.4 mol of AgF; for maximum recovery of aromatics we prefer to use about 0.8 to 1.0 mol and, in some cases, as much as 1.5 mols of AgF per mol of aromatic present in the mixed feed.

A still further and entirely unexpected effect of the amount of AgF present in the extraction system, at constant liquid HF level, is the selectivity of extraction, i. e. the purity of the extract. This surprising result is illustrated by the following data, which will be discussed in more detail hereinafter:

Run	Feed, Percent Aromatics	HF, Vol. Percent on Aromatics	AgF, Mols/Mol of Aromatics	Extract, V. Percent Arom.
3	40	300	0.4	94
4	54	220	1.0	99
6	32	300	1.0	99

It is our opinion that the AgF that is present in excess of the stoichiometric amount tends to "salt out" any physically dissolved hydrocarbons, and therefore increases the selectivity of aromatics separation in addition to making the extraction more complete.

The complex that exists in the extract phase from the treatment of a mixture of aromatic hydrocarbons and non-aromatic hydrocarbon with our liquid HF–AgF treating agent behaves like the complex formed by treating a pure aromatic with the treating agent. The complex is stable in the presence of liquid HF at the temperature of operations normally used in solvent extraction. Of course when operating at temperatures above the boiling point of HF, it is necessary to apply superatmospheric pressure to the system in order to maintain the HF in the liquid state. The extracted hydrocarbons can be recovered from the extract phase by heating the extract phase and distilling off the HF, whereupon the extract and solid AgF remain behind; the solid AgF and extract hydrocarbons are readily separable by decantation, filtration, centrifuging or by distilling off the aromatics. The AgF recovered by this method may be reused in the process.

The extract hydrocarbons may also be recovered from the extract phase by treating said extract phase with water, whereupon the extract hydrocarbons appear as a separate phase which may be decanted from the lower aqueous layer. This latter method of separation is particularly well suited for laboratory operations.

We believe that the complex obtained by the treatment of an aromatic hydrocarbon with AgF in the presence of liquid HF contains three components, namely, for each mol of complex: 1 mol of AgF, 3 mols of aromatic hydrocarbon, and probably at least 1 mol of HF. Although the solubility of AgF in liquid HF is high, even the saturated solution is capable of providing enough HF to form the complex. It is necessary to have an excess of liquid HF present to dissolve the complex that has been formed and to permit its separation as a solution in the liquid HF from the non-aromatic hydrocarbons and the non-complexed aromatic hydrocarbons. This solution consists of liquid HF, the complex, aromatic hydrocarbons in simple solution and non-aromatic hydrocarbons apparently in simple solution; we mean this solution when we speak of the extract phase. Obviously the amount of liquid HF needed will depend somewhat upon the amount of aromatic hydrocarbon that is to be extracted from a mixed hydrocarbon feed. We have found that good phase separation can be obtained when a mixed hydrocarbon is contacted with our treating agent wherein the HF content is about 10 volume percent based on total aromatics in the mixed feed. Amounts of liquid HF up to 1500 volume percent based on aromatics in the mixed feed have been used; in general better phase separation is obtained when using amounts in excess of 1 volume of liquid HF per volume of aromatics to be extracted.

Non-aromatic hydrocarbons are only very slightly soluble in liquid HF; they are somewhat more soluble in liquid HF containing the aromatic-AgF-HF complex. Apparently the complex solubilizes both aromatic hydrocarbons and non-aromatic hydrocarbons so that more of these hydrocarbons can be taken up by the liquid HF than would be predicted by the solubility of the hydrocarbons in pure liquid HF. However, this solubilizing effect at constant AgF level appears to be a function of the concentration of the complex in the liquid HF because, surprisingly enough, we have discovered that the amount of non-aromatic hydrocarbon present in the extract hydrocarbons is lower at large liquid HF usage than at small liquid HF usage. For example at an AgF usage of 0.17 mol, 20% of liquid HF based on aromatics in mixed feed produced an extract containing 15% of non-aromatics. At 300% of liquid HF usage the extract hydrocarbons contained only 5% of non-aromatics. The amount of non-aromatics present in the extract hydrocarbons at the same AgF concentration can be reduced to an ordinarily unobjectionable amount of 2–3% in a single stage by using about 500% or more of liquid HF based on total aromatics in the mixed feed. While our process is operable with as little as 10 volume percent and as much as 1500 volume percent or more of liquid HF based on total aromatics in a mixed hydrocarbon feed, we prefer to use between about 75 and 600 volume percent of liquid HF and when using about 0.8 or more mols of AgF, we prefer to use between 75 and 300 volume percent. We prefer to use substantially anhydrous liquid HF, i. e. HF containing not more than about 1 or 2% of water.

Temperatures as low as −60° F. may be used if the resultant increase in viscosity is not considered to be disadvantageous. At higher temperatures, for example 250–300° F., the HF catalyzes the isomerization and even cracking of the paraffins and naphthenes normally present in naphthas derived from petroleum sources. In general, we operate between 0° and 160° F. and we prefer to operate at ambient temperatures, i. e. between 30 and about 100° F. In order to keep the HF in the liquid state, sufficient pressure must be maintained on the extraction system to ensure this condition at the temperature of operation. Thus at 160° F., we operate at about 100 p. s. i. g. This latter range of temperatures gives good results and introduces the least number of complications into the design of the process equipment.

For best results the feed stock and the solvent should

be contacted for a time long enough to permit maximum recovery of aromatics by the particular amount of AgF present in the treating agent. The length of time needed for this amount of contacting in large part will depend upon the efficiency of the contacting device. When operating at ambient temperatures, contacting times in excess of the minimum necessary for desired amount of recovery are not harmful. In general, we have found that with efficient mixing, good results can be obtained at contact times between about five minutes and six hours.

Organic-sulfur compounds, such as are normally present in most petroleum naphthas, form complexes with AgF in the presence of liquid HF. These complexes are more stable than the AgF-aromatic complexes and are more difficult to decompose. However, heating the complex to 400–500° F. will drive off HF and sulfur compounds and thus dissociate the complex. The AgF-sulfur compound complexes are solid materials somewhat similar in appearance to the asphaltic constituents of crude oil. These complexes tend to emulsify the extract phase into the raffinate phase, rendering a separation between the two phases difficult, and in some cases, virtually impossible by ordinary methods. (The solid material can be removed by precoat filtration or by centrifuging.) The larger the percent of sulfur present in the naphtha to be treated, the more likely it is that difficulty in separation will be encountered and the more difficult the separation will be in itself. Even when the sulfur compounds do not markedly interfere with the separation, a sludge-like material may be present in the extract phase (or even in the raffinate phase) which will interfere with the recovery of the aromatics (or the non-aromatics free of AgF). To illustrate, a virgin naphtha containing about 23% of toluene and xylenes and having a total sulfur content of 0.32 weight per cent, was contacted at about 70° F. with 400 volume percent of liquid HF and 1 mol of AgF per mol of aromatics. It was found impossible to withdraw the mixture from the reactor. When the reactor was opened, it was found to contain a pasty mass consisting of the naphtha, liquid HF and AgF. On the other hand, when a sample of the same virgin naptha was desulfurized with liquid HF alone and the essentially sulfur-free naphtha contacted with liquid HF-AgF solvent as above, a clean separation between the raffinate and extract phases was obtained. In another experiment a synthetic mixture of normal heptane and xylenes was increased to a total sulfur content of 0.4 weight percent by the addition of di-n-propyl sulfide; this feed stock was treated with liquid HF-AgF solvent and a fairly clean separation was obtained between the raffinate and the extract phases. However, the raffinate phase contained a considerable amount of finely dispersed particles of AgF-sulfide complex; this material was difficultly removable from the raffinate phase. In general, we prefer to operate on hydrocarbon mixtures which contain essentially no sulfur compounds—on the order of less than .02 weight per cent sulfur. Naphthas containing a sulfur content suitable for our process can be readily obtained by treating high sulfur naphthas with liquid HF or by hydrodesulfurization or by hydroforming or by any other process that removes sulfur without simultaneously removing appreciable quantities of the desired aromatics.

In general, olefins, in the amounts usually present in naphthas that would be desirable feed stocks to our process, do not interfere with separation of the extract phase from the raffinate phase. We have found that the aromatic compounds present are alkylated by the olefins in the feed stock to form alkylaromatics which complex with AgF and which are recovered in the extract phase along with the non-alkylated aromatics. These alkylated aromatics boil above xylenes and can be readily separated from xylenes by simple fractional distillation.

No appreciable formation of alkylfluorides has been observed when treating olefin-containing feed stock. Thus the disadvantage for operation on an olefin-containing feed stock is the loss of some of the more desirable aromatic compounds to higher boiling alkylaromatics. However, these alkylaromatics have high octane numbers and can be used as aviation safety fuel blending stocks; or they may be used as high solvency naphthas.

The phenolic-type materials found in most naphthas derived from thermal or catalytic cracking react with AgF to form complexes which are detrimental to phase separation. Also, these materials increase the difficulty of obtaining pure compounds by simple fractional distillation from the aromatics recovered by our process. However, one or two washes with a concentrated sodium hydroxide solution will reduce these phenolic compounds to a level where no appreciable hinderance to phase separation will take place. Another method of removing these phenolic bodies is to treat the raw naphtha with liquid HF.

Our process may be applied to a mixture of hydrocarbons comprising aromatics, paraffins, naphthenes and olefins which boil in the naphtha range, i. e. below about 450° F. The presence of polyalkylbenzenes and polynuclear aromatics in hydrocarbon distillates boiling above about 450° F. renders very difficult the recovery of individual compounds or a group containing a small number of compounds boiling close together. The feed stock to our process must be free from H_2S and substantially free of organic sulfur compounds, particularly those found in virgin naphthas derived from high sulfur crudes, such as West Texas crude. We prefer that the feed stock contain less than about 0.02 weight percent of sulfur. In general, we have found that a high sulfur naphtha which has been desulfurized by treatment with liquid HF is a satisfactory feed to our process. Naphthas containing appreciable amounts of materials boiling above 450° F. are more difficult to desulfurize by conventional methods to a level at which the sulfur compounds will not interfere with the separation of the feed stock into a raffinate phase and an extract phase. Naphthas boiling below about 325° F. are particularly suitable for our process because they are easily desulfurized and dephenolized and substantially pure C_6, C_7 and mixed C_8 aromatics are readily recovered therefrom.

The presence of olefins in the feed stock is undesirable because of the decrease in the yield of the lower boiling aromatics present in the feed stock by alkylation. The phenolic compounds present in thermally cracked naphthas and in the so-called catalytically cracked naphthas such as from the fluid catalytic cracking, Thermofor catalytic cracking, or Houdry cracking processes interfere with phase separation in our process. Phenolic body-containing cracked naphthas are a suitable feed to our process after treatment for the removal of these materials.

A particularly suitable feed for our process is the naphtha derived from the so-called hydroforming process, i. e. the vapor phase treatment of a virgin naphtha at 850–1050° F. in the presence of hydrogen over a catalyst such as molybdena on an alumina support or a platinum-containing catalyst. The hydroformate from such a process is low enough in sulfur to permit operation without further desulfurization and is so low in olefin that very little of the benzene, toluene and xylenes is degraded to higher boiling alkyl aromatics by alkylation.

Thus by suitable pretreatment to remove interfering materials we can charge to our process materials boiling below about 450° F., and particularly those boiling below 325° F., derived from distillation of petroleum, the thermal or catalytic cracking of naphthas from petroleum, naphthas derived by the hydroforming or hydrodesulfurization of virgin or cracked naphthas, or a mixture of aro-

matics, paraffinics, naphthenics and olefinics derived from any source.

The usual feed stock to our process will contain 50 volume percent or more of non-aromatic material. Where aromatic concentrates are available from super fractionation equipment, feed stock containing 70 or 80% of benzene or toluene or C_8 aromatics may be available. We have found that when operating on feed stocks containing much in excess of 50% of aromatic hydrocarbons, it is desirable to add a diluent to the feed stock prior to the contacting step. The diluent should be a paraffinic and/or naphthenic hydrocarbon or a mixture of hydrocarbons that is low in materials that would interfere with phase separation and that will be readily separable by simple fractional distillation from the individual aromatic hydrocarbons. We prefer to use as diluents paraffinic and naphthenic hydrocarbons of low boiling point since these materials are not isomerized or cracked by the liquid HF at the preferred operating temperatures. Suitable hydrocarbons are pentane, hexane, heptane, cyclohexane, methylcyclohexane, petroleum ether, etc. When operating at low temperatures such as 30° F. the diluents might be higher boiling paraffinic or naphthenic hydrocarbons containing 9, 10 or 11 carbon atoms. However, in general, the feed stocks to our process will not require the use of a diluent. We prefer to operate without diluent since the presence of high percentages of non-aromatic compounds requires the use of more AgF in order to obtain the same percentage extraction and more HF in order to maintain selectivity of extraction.

The non-aromatic hydrocarbons extracted from the feed by the treating agent boil in about the same range as the aromatic hydrocarbons. Their presence decreases the purity of the aromatic hydrocarbons and they must be removed in order to obtain substantially pure aromatics as the final product. We have found that these non-aromatic hydrocarbons can be readily displaced from the extract phase by washing the extract phase with a diluent type hydrocarbon such as pentane, hexane or a 9, 10 or 11 carbon atom hydrocarbon. A single stage washing operation is usually sufficient to reduce the non-aromatic content of the extract phase to a point where nitration grade benzene or toluene can be made by simple fractional distillation of the recovered aromatic hydrocarbons.

Several examples of the types of stock amenable to treatment and the aromatic hydrocarbon recoveries obtainable by our process are set out below. In all cases the contacting was carried out in a carbon steel reactor equipped with a 1725 R. P. M. stirrer. The experimental procedure was to add a quantity of AgF to the reactor followed by liquid HF and then by the aromatic-containing feed stock. The contents of the reactor were stirred for between 15 and 60 minutes at the selected temperature of contacting; at the end of the contacting time the contents of the reactor were allowed to settle for 2 hours. The lower extract phase was withdrawn into a vessel containing crushed ice; the hydrocarbons from the decomposed extract phase were decanted away from the aqueous layer. The hydrocarbons were washed with caustic to eliminate traces of HF and then were distilled in a 30-plate laboratory column to recover the various fractions. These fractions were then analyzed by ultraviolet and infrared absorption methods. The purity and the compositions of the fractions was determined by a combination of ultraviolet and infrared analysis, boiling point, specific gravity and refractive index.

The raffinate phase was washed with aqueous caustic to remove entrained HF and was then analyzed for aromatic content.

Run 1

A West Texas heavy virgin naphtha having a boiling range of 273° to 449° F., a total sulfur content of 0.32 weight per cent and a refractive index n_D^{20} of 1.4329 was contacted with 100 volume percent of liquid HF, based on naphtha, at 65° F. for 60 minutes. The contents were settled and the extract phase and raffinate phase withdrawn separately. The extract phase consisted almost entirely of organic sulfur compounds. The raffinate had a sulfur content of 0.02 weight per cent and a refractive index of 1.4332. Insofar as could be determined, substantially no aromatic hydrocarbons had been removed by the liquid HF treatment.

The desulfurized West Texas naphtha, which contained about 23 volume percent of C_8 aromatics was contacted with 400 volume percent of liquid HF based on aromatics and 1 mol of AgF per mol of aromatic therein at 65° F. for 1 hour. The extract phase was decomposed and the hydrocarbons recovered. The analysis of these hydrocarbons indicated that they contained 98% of aromatics and 2% of non-aromatics; the refractive index of the total hydrocarbons extracted was 1.4982. For this one-contacting stage treatment the extraction of aromatic hydrocarbons was about 95%. The hydrocarbons recovered from the raffinate phase contained about 2% of aromatics.

It was noticed that a very slight amount of a sludge-like material was present in the extract phase. The amount of this material was so small that there was no interference with phase separation. It is believed that this sludge was a complex of AgF and organic sulfur compounds.

Run 2

The benzene cut of a low-sulfur virgin naphtha having a refractive index of 1.3892 and containing about 10% of benzene was contacted with 1,300 volume percent of liquid HF, based on benzene, and 1 mol of AgF per mol of benzene at 70° F. It was found that 78% of the benzene in the feed was extracted by this single-stage contacting.

Run 3

A mixture of 10 volume percent of ortho-xylene, meta-xylene, para-xylene and ethylbenzene, respectively, and 60 volume percent n-heptane was contacted with 300 volume percent of liquid HF, based on aromatics, and 0.4 mol of AgF per mol of C_8 aromatic at 71° F.

The hydrocarbons in the extract phase contained about 6% of n-heptane. The total aromatic extraction was 89%. The hydrocarbons in the raffinate phase contained about 7% of C_8 aromatics.

Run 4

The feed to this run was a 93–303° F. boiling point cut derived from the distillation of a hydroformate from the hydroforming of a mixed virgin heavy naphtha at 980° F. over a molybdena on alumina catalyst. This cut contained a total of 54% of benzene, toluene and C_8 aromatics, about 3% of olefins and about .01% of sulfur. The cut was contacted with 220 volume percent of liquid HF, based on aromatics, and 1 mol of AgF per mol of aromatics at 64° F.

The hydrocarbons in the extract phase contained about 1% of nonaromatics. The removal of aromatics to the extract phase was 98%. The hydrocarbons in the raffinate phase contained about 2% of aromatics.

Run 5

A mixture of 20 volume percent meta-xylene, 20 volume per cent para-xylene and 60 volume percent n-heptane was contacted with 300 volume percent liquid HF, based on xylene, and 0.5 mol of AgF per mol of xylene at 50° F. for 60 minutes. The hydrocarbons in the extract phase contained about 7% of n-heptane. The aromatic extraction was about 98%. The hydrocarbons in the raffinate phase contained less than 1% of xylenes.

Run 6

The charge to this run consisted of 8% each of ortho-xylene, meta-xylene, para-xylene and ethylbenzene, 60%

of n-heptane, 4% of octene-1 and 4% of cyclohexene. The feed was contacted with 700 volume percent of liquid HF based on C_8 aromatics and 1 mol of AgF per mol of aromatics at 72° F. for 60 minutes. A clean separation was obtained between the extract phase and the raffinate phase.

The hydrocarbons from the extract phase contained about 1% of non-aromatics. The hydrocarbons in the raffinate phase within the limits of experimental determination contained no aromatics. Thus in this run the aromatic recovery from non-aromatics was substantially complete in one contacting, even in the presence of olefins.

Distillation of the hydrocarbons from the extract phase showed an amount of higher boiling material to be present in amount about equal to the olefins present in the feed stock; this indicates that the octene-1 and cyclohexene reacted with the aromatics under the influence of liquid HF to form higher boiling polyalkyl aromatics.

Run 7

The feed in this run consisted of 40% benzene and 60% n-heptane. This feed was contacted with 300 volume percent liquid HF, based on benzene, and 0.18 mol of AgF per mol of benzene at 70° F. for 60 minutes.

The hydrocarbon in the extract phase contained 5% of n-heptane. The benzene extracted was 57% of that present in the feed stock. The hydrocarbon in the raffinate phase contained 23% benzene.

Runs 8–10

Three runs were made to determine the effect of liquid HF usage on the non-aromatic content of the hydrocarbons in the extract phase. The feed stock in all runs was p-xylene, 20%; ethylbenzene, 20%; and n-heptane, 60%. In all runs 0.17 mol of AgF per mol of aromatic was used. The mixture was stirred for 1 hour at 70° F. and was allowed to settle for 2 hours. The phases were separated; in each run clean-cut phase separation was obtained. The hydrocarbons were recovered from each phase and were analyzed for aromatic and non-aromatic content. In all runs the aromatics extracted corresponded to 50% of the aromatics in the feed, i. e. the theoretical amount based on AgF present.

The hydrocarbon distribution in the extract phase varied with the amount of liquid HF used. The analysis on volume percent of the extract hydrocarbons for each run follow. The liquid HF in volume percent used is based on C_8 aromatics in the feed.

Run	HF	Aromatics	Non-Aromatics
8	300	95	5
9	50	91	9
10	20	85	15

The above results were startling as we had expected that the percentage of non-aromatics would increase with HF usage by virtue of simple solution in the extract phase. We explain this unexpected large inverse effect of HF usage on non-aromatic content in the extract as follows: The solubilizing effect of the organic complex is overcome by dilution with HF faster than the increase in total amount of non-aromatics in the extract phase by simple solution. We do not intend to be bound by the above explanation of this phenomenon.

In the case of Run 8, it would be possible to decrease the nonaromatic content of the extract oil to 1% or less by increasing the amount of AgF to 1 mol per mol of aromatic.

Two diagrammatic illustrations of commercial embodiments of our process are given herein.

Figure 1 shows the removal of aromatics from a substantially sulfur-free, but olefin-containing feed stock.

Figure 2 shows the recovery of aromatics from a high-sulfur-content virgin naphtha containing substantially no olefins.

The feed to the embodiment illustrated in Figure 1 consists of a debutanized hydroformate having an end point of 325° F. This hydroformate contains about 55% of benzene, toluene and C_8 aromatics, and about 3% of olefins. A typical sulfur content for this hydroformate is about 0.01 weight percent.

The feed from source 11 passes through line 12 into mixer 13. In mixer 13 the feed is thoroughly contacted with the extract phase from a previous contacting step to be described later; this extract phase—consisting of liquid HF, complex, an excess of AgF and dissolved non-aromatic hydrocarbons—is passed into line 12 by way of line 14. Mixer 13 is provided with a heat exchanger 16 which permits the temperature of contacting to be maintained at the desired point. In this illustration contacting is carried out at 75° F. and at about 25 p. s. i. g. for about 15 minutes.

From mixer 13 the mixed feed-solvent passes through line 17 into settler 18. In settler 18 the mixed feed-solvent separates into a raffinate phase consisting mainly of non-aromatic hydrocarbons and a small percentage of aromatic hydrocarbons and an extract phase consisting of liquid HF, complex, excess AgF and minor amounts of non-aromatic hydrocarbons. The raffinate from settler 18 is withdrawn through line 19 and is passed into line 21.

Liquid HF from source 22 is passed through line 23 into vessel 24 where it meets AgF from source 26 and line 27 and also recycled liquid HF–AgF solution. In order to recover the aromatics present in the feed in the least number of stages we use 1.0 mol of AgF in this particular illustration, all of which will be present in mixer 31. The liquid HF must be present in an amount great enough to form the complex and to dissolve the complex once formed. More than this amount is desirable as phase separation and aromatic selectivity are facilitated by a larger volume of liquid HF. In this particular illustration we use 200 volume percent of liquid HF based upon the aromatics in the feed stock charged to the process. The liquid HF–AgF solution from vessel 24 passes into line 21 where it meets the raffinate phase from settler 18 and on into mixer 31. Mixer 31 is provided with a heat exchanger 32 for control of the temperature of contacting; herein we operate at about 75° F., the same as that used in the first contacting stage in mixer 13. The liquid HF–AgF solvent and the first raffinate phase are intimately contacted for about 15 minutes in mixer 31. From mixer 31 the mixture passes through line 33 into settler 34. In settler 34 a second raffinate phase containing little or no aromatic hydrocarbons is separated from the extract phase. This second raffinate phase from settler 34 passes through line 36 into stripper 37 which is provided with reboiler 38. In stripper 37 the HF dissolved in the second raffinate phase is removed overhead through line 39; stripper 37 may be operated at about 200 to 400° F. at about 25 to 150 p. s. i. g. In heat exchanger 41 the HF is condensed to a liquid and may be recycled to the process through line 42. Some low boiling material may azeotrope with the HF and this may be recycled along with the HF. However, if this material is not wanted in the extraction step, it can be removed by a settling operation (not shown) from the liquid HF and sent to the non-aromatic product. The non-aromatic portion of the feed stock passes out of stripper 37 through line 46 to storage not shown. These non-aromatic hydrocarbons are almost entirely isoparaffins of high octane number and are valuable as gasoline blending material. The very slight fluoride content thereof can be eliminated by percolation through bauxite.

From settler 34 the extract phase is sent to the first contacting stage through line 14. By this two-stage countercurrent contacting procedure, we are able to recover substantially all the aromatic hydrocarbons present in the feed stock.

From settler 18 the extract phase is passed through line 51 into line 52 where it meets pentane from source 53. From line 52 the extract phase-pentane mixture passes into mixer 54. The pentane usage will be dependent upon the percent of non-aromatics in the extract phase. We have found that particularly good results are obtained when between 50 and 200 volume percent based on total hydrocarbons present in the extract phase is used. From mixer 54 the pentane-extract phase mixture passes through line 56 into settler 57. From settler 57 a raffinate phase consisting of pentane and substantially all the non-aromatics present in the extract phase from line 51 is withdrawn by line 58. The material in line 58 may be withdrawn from the system through valved line 59 or a portion may be recycled to the washing step through valved line 61 and line 62. In order to avoid a buildup of interfering non-aromatic hydrocarbons in the washed extract phase, we prefer that the contaminated pentane be discarded to gasoline blending stock.

From settler 57 the washed extract phase passes through line 66 through heat exchanger 67 and line 68 into vessel 69. Vessel 69, commonly called a decomposer, is provided with a heat exchanger 71 and a number of bubble trays in order to obtain some fractionation. In decomposer 69 the HF and pentane are passed overhead through line 74 and are condensed by heat exchanger 75. The HF-pentane mixture passes from line 76 into settler 77 where two phases are formed. The upper pentane layer passes out through line 78 to gasoline blending stock. The lower HF layer passes out of settler 77 through line 79. The decomposer 69 is maintained at a top temperature below the boiling point of benzene in order to keep all the aromatics in the liquid state in decomposer 69. We have found that a suitable top temperature for the operation of decomposer 69 is between about 100 and 140° F., at atmospheric pressure operation. Higher temperatures may be used if the decomposer is operated at super atmospheric pressure. The bottom temperature of decomposer 69 can be between 200 and 500° F. and about the mid-boiling point of the aromatics is a suitable temperature.

In the bottom of decomposer 69 a slurry of solid, finely divided AgF and aromatic hydrocarbons is formed. This slurry passes out of decomposer 69 through valved line 81 into filter 82. Filter 82 may be a plate and frame or a rotary filter or any type which can be made of liquid HF-resistant materials and HF-vaportight. A filter of the Sweetland type is suitable for this type of operation. In this flow sheet we show only one filter. However, normally two or more filters will be used in order to permit continuous operation and the presence of additional filters is to be understood in this particular illustration of our process. Filter 82 retains the solid AgF and the aromatics pass out through valved line 83.

Liquid HF from settler 77 passes through valved line 79 into filter 82; the AgF in the filter is dissolved by the liquid HF and the liquid HF–AgF solution passes out of filter 82 through valved line 86 and is recycled to vessel 24 through line 87.

From filter 82 the aromatics pass through valved line 83, through heat exchanger 91 and through line 92 into fractionator 93, which fractionator is equipped with reboiler 94. In fractionator 93 nitration-grade benzene is taken overhead through line 97 to storage not shown. The remaining aromatics pass out of the bottom of the fractionator 93 through line 99, heat exchanger 101 and line 102 into fractionator 103.

Fractionator 103, equipped with reboiler 104, separates the aromatics from line 102 into a nitration-grade toluene fraction, taken overhead through line 106 to storage not shown; and a bottoms fraction consisting of C_8 aromatics and higher boiling polyalkyl aromatics.

The bottoms from fractionator 103 pass out through line 107, heat exchanger 108 and line 109 into fractionator 111, which is equipped with reboiler 112. The C_8 aromatics, consisting of o-xylene, m-xylene, p-xylene and ethylbenzene pass out of fractionator 111 through line 114 to storage not shown. From the bottom of fractionator 111 through line 116 higher boiling polyalkyl aromatics are withdrawn. These higher boiling aromatics were formed by the alkylation of lower boiling aromatics with the olefins present in the feed by the catalytic action of the liquid HF.

This embodiment of our invention shows how simply we are able to separate benzene, toluene and C_8 aromatics from a mixed hydrocarbon and by simple fractional distillation recover nitration-grade benzene and toluene and mixed C_8 aromatic hydrocarbons separately.

In Figure 2 is illustrated the recovery of benzene, toluene and C_8 aromatics from a 340° F. end-point virgin naphtha which contains enough organic sulfur compounds to prevent the separation of two phases when said naphtha is treated directly with liquid HF-AgF solvent. In this case the feed stock is a debutanized virgin naphtha, derived from a West Texas crude, containing about 0.2 weight per cent of sulfur and about 25% of benzene, toluene, xylenes and ethylbenzene and substantially no olefins. This feed from source 211 is passed by way of line 212 into extraction tower 213 at a point somewhat above the bottom of the tower. Liquid HF from source 217 in an amount about 30 volume percent based on feed is passed through line 218 into tower 213 at a point somewhat below the top of the tower. In order to insure good contacting, tower 213 may be packed with Raschig rings, Berl saddles, etc., or may be equipped with modified bubble trays. In this particular operation we prefer to operate with the interface somewhat below the point of entry of the liquid HF. Tower 213 is provided with heat exchangers 214, 215 and 216 to permit control of the temperature of operation. In this instance, we operate at about 75° F. and about 25 p. s. i. g.

The extract phase—containing HF, organic sulfur compounds and some feed stock—passes out of the bottom of the tower through line 219 into heat exchanger 224 and then through line 226 into a decomposer 228, which decomposer is equipped with an internal heater 229. The temperature maintained in decomposer 228 is great enough to decompose the complex formed by the sulfur compounds and the HF. A suitable temperature is between about 200° F. and 500° F.; superatmospheric pressures are maintained on the decomposer in order to prevent carrying over the lower boiling of the organic sulfur compounds with the HF vapors. The vaporized HF passes out of decomposer 228 through line 232 through condenser 233 and the liquid HF is recycled to the desulfurization step through line 234 and line 218. The organic sulfur compounds pass out of decomposer 228 through line 237 to storage not shown. In order to improve the selectivity of the extraction step for sulfur compounds and decrease the amount of hydrocarbons contained in the extract phase, some of the sulfur compounds may be recycled through valved line 238 to extraction tower 213 at a point near the base of the tower. (A more detailed description of the above desulfurization process is given in U. S. 2,450,588.)

The raffinate phase from tower 213 contains about 0.01 weight per cent of sulfur and contains substantially all the aromatics present in the feed. The raffinate phase passes out of tower 213 through line 241 into extraction tower 243 at a lower point of said tower, e. g., about one-fifth of the way from the bottom thereof. Tower 243 is equipped with heat exchangers 246, 247 and 248 which permit the tower to be operated at any temperature between 30° F. and 100° F. In this example we operate at about 80° F. and 25 p. s. i. g. Extraction tower 243 may be constructed like extraction tower 213. Liquid HF from source 251 is passed through lines 252 and 254 into vessel 256. Solid AgF from source 261 is passed through line 262 into vessel 256 wherein it is dissolved in the liquid HF. The liquid HF-AgF treating agent

is passed from vessel **256** through line **263** and manifolded line **264** into extraction tower **243**. We prefer to charge the liquid HF-AgF solution near the top of the tower; however, if desired, the solvent may be passed into the tower at various points along its height. The amount of liquid HF used in this illustration is about 300 volume percent based on the volume of aromatics in the desulfurized feed oil, and 1.1 mols of AgF are used per mol of aromatic present in said desulfurized feed oil. Raffinate phase passes out of tower **243** through line **267** into heat exchanger **268** and through line **269** into stripper **271**; this stripper is equipped with heat exchanger **272**. In the stripper **271** the HF and some azeotroped low boiling hydrocarbon pass out of the stripper through line **274** and are condensed in heat exchanger **276**. The liquid HF and low boiling hydrocarbon from exchanger **276** pass through line **278** back to the aromatic separation tower through line **254**. If desired, the hydrocarbons can be separated from the liquid HF by a settling operation (not shown) and sent to the non-aromatic product.

The non-aromatic hydrocarbons pass out of the bottom of stripper **271** through line **282** to storage not shown. These hydrocarbons may be used for gasoline blending purposes or sent to a hydroforming operation since the absence of aromatics increases their value for hydroforming feed stock.

Extraction tower **243** is operated in such a way that substantially all the aromatics present in the desulfurized feed oil are removed by the treating agent and passed out of the tower in the extract phase by way of line **294** into a washer **296**. Washer **296** is an elementary packed tower. Pentane from source **298** is passed through line **299** into washer **296** at a point near the bottom thereof. As the pentane passes up through the tower against the descending stream of extract phase from tower **243**, the non-aromatics in the extract phase are displaced by the pentane so that the washed extract phase which passes out of the bottom of the washer through line **302** contains substantially only pentane as the non-aromatic hydrocarbon. The pentane passes out of the top of the tower through line **304** and is discarded to gasoline blending stock through valved line **306**; some of this contaminated pentane may be recycled to the washing step through valved line **307**. We prefer to operate without recycle in order to reduce the amount of higher boiling non-aromatics present in the washed extract phase.

The washed extract phase passes through line **302** through heat exchanger **309** and line **311** into decomposer **312**. Decomposer **312** is provided with an internal heat exchanger **313** and several bubble trays in order to obtain some fractionation. In decomposer **312** the complex is destroyed by boiling off the HF. The top temperature maintained in decomposer **312** is preferably high enough to vaporize all the HF and the pentane, i. e. above 100° F. at atmospheric pressure operation and yet low enough to retain the benzene in the decomposer. The bottom temperature should be between about 200 and 400° F.

The aromatics and the solid finely divided AgF are present in the bottom of decomposer **312** in the form of a slurry, which slurry passes out of the decomposer through valved line **318** into filter **319**. Filter **319** may be any type of HF-resistant, HF-vapor-tight filter of the plate and frame type, rotary type, etc. We prefer to use a filter of the Sweetland type. The aromatics pass out of filter **319** through valved line **321** through heat exchanger **322** and line **323** into fractionator **324**.

The HF and pentane vapors pass from decomposer **312** through line **331** and are condensed by heat exchanger **332**. The HF-pentane mixture from line **333** passes into settler **334** where two phases are formed. The upper pentane layer passes out through line **335** to gasoline blending stock. The lower HF layer passes out through line **336** into filter **319** and dissolves the AgF contained therein. The liquid HF-AgF solution passes out of filter **319** by way of valved line **336** and is recycled to the aromatic recovery tower by way of line **337** and line **264**. While we have illustrated here only one filter, it is to be understood that a commercial operation would utilize two or more filters intermittently in order to have continuous operation.

In tower **324** the aromatics are fractionated into a nitration-grade benzene overhead and a toluene-C_8 aromatic bottoms. Fractionator **324** is equipped with a reboiler **326**. Nitration-grade benzene passes out of tower **324** through line **328** to storage not shown.

The bottoms from tower **324** pass out via line **331** through heat exchanger **332** and line **333** into another fractionator **336**, which fractionator is equipped with a reboiler **337**. Fractionator **336** produces a nitration-grade toluene overhead which passes through line **342** to storage not shown. The C_8 aromatics consisting of xylenes and ethylbenzene are withdrawn as a bottoms product from fractionator **336** through line **344**.

In order to improve the selectivity of the extraction and decrease the amount of non-aromatics in the extract phase, we can recycle some of the aromatics from line **321** to the bottom of tower **243** by a line not shown.

In the case of feed stocks containing appreciable amounts of sulfur, the sulfur compound-AgF complex will gradually build up in the system, when operating on a "no aromatic overhead" type of aromatic complex decomposition procedure. The sulfur compound complex will be carried along with the AgF in the system and reduce the effective amount of AgF therein. Periodically, the AgF and sulfur compound complex can be dissolved out of the filter **82** and the liquid HF solution sent to decomposer **69**—in a blocked out operation. Here the major part of the HF is taken overhead and then the temperature in the decomposer is raised to between 400 and 500° F. At this temperature the sulfur compound complex is decomposed and the sulfur compounds together with any remaining HF pass overhead through lines **74**, are condensed in exchager **75** and pass out of the system by a line not shown. A new cycle of operation may then be begun by dissolving the AgF in the decomposer with liquid HF.

It is to be understood that the above described embodiments of our invention are submitted by way of example and do not include all the variations which can easily be made by one skilled in the art; such variations will be dependent upon the particular feed stock used and the operating conditions desired. For instance, in Figure 1 we have shown multi-stage batch countercurrent extraction, and in Figure 2 we have shown a continuous countercurrent tower type extraction. Either type of operation could be used for any feed stock. Indeed in certain cases, single-stage batch extraction may be adequate. The particular type of contacting apparatus will be dependent upon the feed stock and upon the individual preferences of the designer of a particular plant.

We have shown one method of recovery of the solid AgF from the decomposition of the complex. We do not wish to be bound by this method as the only method for this recovery. For example, the decomposer can be operated at such a temperature that all of the aromatic product is taken overhead and the hydrocarbons separated from the liquid HF by decantation. The pentane can be readily separated from the armomatics by simple fractional distillation. The residual AgF in the decomposer is dissolved in liquid HF and the solution recycled to vessel **24** via line **87**. Continuous operation is achieved by intermittent use of two or more external reboiler vessels. Alternatively, the solid AgF remaining in the decomposer can then be removed in the form of a slurry in a higher boiling paraffinic or naphthenic hydrocarbon, such as C_{10} or C_{11} mixed paraffins. This slurry can be contacted with a stream of liquid HF at low temperature—to prevent isomerization or cracking of the paraffin—and the AgF dissolved out of the slurry. The liquid HF-AgF

solution can then be recovered by settling and decantation from the slurrying hydrocarbon and recycled to the aromatic recovery step. Still other methods of recovering the solid AgF can very readily be devised, and we intend to include such methods within the scope of our invention.

We claim:

1. An extraction process which comprises (1) contacting a liquid feed consisting of aromatic hydrocarbons and non-aromatic hydrocarbons boiling in the naphtha range and substantially no olefins, organic-sulfur compounds and phenolic compounds, under substantially anhydrous conditions, at a temperature between about 0° F. and 160° F., with a liquid agent consisting of between 0.8 and 1.5 mols of silver fluoride per mol of aromatic hydrocarbon in said feed and at least 200 volume per cent, based on aromatic hydrocarbons in said feed, of substantially anhydrous liquid hydrogen fluoride, (2) separating a raffinate phase from an extract phase and (3) removing HF and AgF from said extract phase to recover an extract consisting of at least 98 volume per cent of aromatic hydrocarbons.

2. The process of claim 1 wherein said AgF usage is about 1 mol per mol of aromatic hydrocarbon in said feed.

3. The process of claim 1 wherein said HF usage is between about 300% and 700% based on aromatic hydrocarbon in said feed.

4. The process of claim 1 wherein said feed is a naphtha produced from the liquid product of the catalytic reforming of naphtha in the presence of hydrogen.

5. The process of claim 1 wherein said temperature is between about 30° F. and 100° F.

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