REMOVAL OF AROMATIC COMPOUNDS FROM COKE OVEN GAS

Calvin J. Hess

William M. Perry
This invention relates to the removal of aromatic compounds from coke oven gas, and more particularly, to the recovery of the aromatic compounds in a high state of purity.

It is a major object of the invention to recover a benzene product having a high freeze point.

Another object is to recover a pure benzene product from coke oven gas by a method which utilizes conventional gas scrubbing equipment.

A further object is to recover a high-freeze point benzene product from coke oven gas wherein additional purifying steps, ordinarily required for such recovery, are eliminated.

In coke oven gas, resulting from the distillation of coal in the manufacture of coke, light oils contained in the gas are ordinarily removed from the gas by means of a light oil scrubber. After the tar, ammonia, phenol and substantially all of the naphthenes have been removed from the gas, the gas enters a scrubber, or scrubbers, wherein light oil is removed from the gas stream. When the gas enters the scrubber, it contains, besides light oil, considerable amounts of aliphatic and aromatic compounds.

The aliphatics so contained comprise, primary, certain paraffins and olefins, while the aromatics are represented by naphthenes such as cyclohexane and methy1 cyclohexane. The aromatic compounds contained in the gas at this point are mono-cyclical, except for possibly trace amounts of naphthenes, and are represented by benzene, toluene, and xylene, known in the trade as BTX. By far, the greater percentage of the BTX is in the form of benzene.

In prior practice, the coke oven gas has been treated in the light oil scrubber by countercurrent washing, or scrubbing, with a hydrocarbon wash oil, familiarly known as straw oil. The function of the straw oil is to absorb and remove the aromatics from the gas. For certain industrial uses, the light oil aromatics recovered in this manner are quite satisfactory. However, with known scrubbing practices, a clean cut separation between aromatics on the one hand, and aliphatics and aromatics on the other, is never attained, as straw oil tends to absorb some of the aliphatics and naphthenes. Certain aliphatics and aromatics, i.e. benzene contaminants, cannot be distilled from benzene because they form azoethers with benzene and the said azoethers have boiling points close to benzene. Table 1 lists some of these azoethers.

### Table 1

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Azeotropic Composition</th>
<th>Benzene, percent</th>
<th>Azeotropic Builing Point, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>53.0</td>
<td>59.0</td>
<td>77.4</td>
</tr>
<tr>
<td>Methy1cyclohexane</td>
<td>90.6</td>
<td>90.0</td>
<td>74.9</td>
</tr>
<tr>
<td>2,3-dimethyl pentane</td>
<td>72.5</td>
<td>75.0</td>
<td>76.5</td>
</tr>
<tr>
<td>2,4-dimethyl pentane</td>
<td>87.1</td>
<td>48.5</td>
<td>70.2</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>9.7</td>
<td>59.8</td>
<td>86.1</td>
</tr>
</tbody>
</table>

Many present day industrial requirements for benzene, as well as for toluene and xylene, as, for example, in the production of aniline, styrene, etc., require an aromatic material of high purity. In light oil scrubbing practice with straw oil, the benzene product obtained therefrom will have a freeze point not higher than 4.8 °C. average. Because the benzene market today requires a larger percentage of high quality product — benzene having a freeze point of 5.3 °C., or above — it has become increasingly difficult for the producer of benzene from coal to meet present day requirements, with the methods and equipment which are a well-known part of a coke oven by-product plant. The difficulty begins with the scrubbing operation, for the prior methods of scrubbing will not produce a crude BTX from which a refined benzene of high freeze point can be produced, with the conventional refining steps to be found in most coke works. The foregoing applies to toluene production, as well, although toluene is generally marketed under different quality specifications.

We have found that by scrubbing coke oven gas with certain glycols, a light oil product can be obtained which is substantially free of aliphatics and alicyclics, and from such light oil a benzene of high purity is obtainable. If thiophene is present in the benzene at this point, thiophene can be removed by a relatively inexpensive subsequent step, as will be explained, so that the production of a benzene having a freeze point of 5.4 °C. is entirely feasible with our method.

Essentially, the method is one in which a coke oven gas is introduced into a light oil scrubber, and contacted therein counter-currently with a glycol of the class which we shall refer to as polyoxyalkylene glycol terminal monoether. A quantity of water is mixed with the glycol.

By scrubbing at low temperature and pressure, or at atmospheric pressure, a light oil product can be obtained which has a much lower analysis of the usual contaminants found in light oil than that produced by prior scrubbing practice.

The type of scrubbing medium which may be used to effect efficient separation of the aromatics from the coke oven gas, is typified by a class of polyoxyalkylene glycols which have a terminal monoether group. These compounds have the following constitutional formula:

\[
\text{HO}-\left(\text{CH}_2-\text{CH}_2\text{O}\right)_x-\left(\text{CH}_2-\text{CHCH}_2\text{O}\right)_y\text{CH}_3+1
\]

The compounds of this class have average gram molecular weights ranging from about 250 to 1000. The \( x \) and \( y \) components occur in about equal molar concentrations and in a block and/or random distribution manner. The terminal alkoxy group, wherein \( n \) may be an integer of from 1 to 5, includes the butoxy, propoxy, ethoxy, etc. forms. The viscosity of this class of compounds ranges from about 55 to 300 Saybolt Universal seconds at 100 °F.

The glycol is mixed with about 1 to about 10 weight percent of water, and introduced into the scrubber, preferably in a downwardly direction, where it meets incoming coke oven gas in countercurrent fashion. The scrubbing operation is performed at atmospheric temperature or higher, preferably in a range of from about 20 °F. to about 120 °F. The pressure in the scrubber may be atmospheric, or slightly higher, but preferably not to exceed 25 pounds per sq. in. gage.

In prior methods of scrubbing, the varying composition of the gas had a direct effect on the quality of the resultant light oil product. This was so due to the low degree of selectivity of the straw oil absorbent for aromatic aromatics and non-aromatics. In treating a gas relatively high in non-aromatics with straw oil, a greater amount of non-aromatics find their way into the light oil product. In our process, the light oil product will contain a low amount of non-aromatics regardless of the amount of these contaminants in the gas before treatment. In the drawings:

FIG. 1 is a flow diagram of a light oil scrubber located...
in a coke oven by-product line immediately following the final coolers, and subsequent light oil refining steps.

FIG. 2 is a flow diagram indicating testing procedure in making comparative light oil recovery tests.

The following example describes one method by which our invention has been performed continuously for recovering light oil, and ultimately, a refined benzene product, from coke oven gas.

Referring to FIG. 1, coke oven gas, from which essentially all of the tar, ammonia, phenol and naphthalene have been removed, is led from final cooler 1 through line 2 and introduced into scrubber 3 under the normal pressure of the gas main. The gas enters the scrubber at a rate of about 500 cu. ft./sec. The absorbing or scrubbing medium is composed of a solution of a polyoxyalkylene glycol monoether and three weight percent of water. The specific glycol monoether used in this case is the butoxy form of a polyoxyethylene-polyoxypropylene glycol monoether polymer. This compound can be obtained under the trade name of Ucon 50-HB-100, and is manufactured by Union Carbide Chemicals Co. The scrubbing mixture passes through sprays 4 and contacts the upflowing gas. During the scrubbing section, the scrubbing liquid removes aromatics from the gas, and the temperature maintained in the scrubber is about 20-30° C, while a pressure of about 26 to 35 inches of water is maintained. The de- aromatized gas leaves the scrubber at 32. This gas still contains alyphatics and naphthenes. The liquid collected at the bottom of the scrubber is withdrawn at line 5. This liquid, benzolized absorber, contains scrubbing solution, forrurnings, primary light oil and secondary light oil. At this point, the scrubbing operation has been completed, and the valuable benzene-toluene-xylene (BTX) has been separated from the coke oven gas.

However, in order to obtain a refined benzene, or toluene and xylene, product, it is necessary to process the benzolized absorber through a series of additional steps.

Referring again to FIG. 1, the liquid mixture from scrubber 3 is directed through line 5 via heat exchanger 6 to stripping column 7, wherein the total light oil, i.e., hydrocarbon mixture, is stripped from the glycol monoether. The glycol monoether, having a relatively high boiling point, remains as liquid in the still, and is withdrawn from the bottom of column 7, through line 8 and heat exchanger 6 to storage tank 30, from whence it may be withdrawn through line 31, and, when mixed with the proper amount of water, introduced into scrubber 3 for the scrubbing of additional coke oven gas.

The total light oil leaves column 7 via pipeline 9 and enters column 10 wherein the secondary oil (benzene, toluene, and xylene) is separated from the primary oil (cannabin, indene, naphthenol, etc.). The secondary oil or crude BTX leaves column 10 via line 12 and enters forrerun removal column 13. In column 13, the forrerunnings (carbon disulfide, cyclopentadiene, etc.), are separated from the BTX by distillation and are removed via line 14. The forrerun-free BTX is withdrawn from column 13 via line 15 and is pumped to agitator 16 by way of valve 15. In the agitator 16, the BTX is washed with 66° Bé sulfuric acid to remove olefins and thiophenes. The acid-washed BTX is then neutralized by washing with an 18% by weight aqueous solution of sodium hydroxide in the same agitator. The neutralization step is followed by a water wash. After discharging acid sludge, waste caustic, and water, in turn, the bottom of the agitator, by means of valve 17 and line 19, the refined BTX is withdrawn via line 18 and sent to residue column 20.

During the sequence of operations in agitator 16, the main, forrerun-free, BTX stream is diverted into agitator 16 which acts as a reservoir for the incoming BTX while the treating steps are being performed in agitator 16; in addition, the residues are being removed from agitator 16 and treated BTX is being pumped to residue column 20. After these operations are completed, the main stream is again directed to agitator 16, and the same sequence of steps is performed in agitator 16, with agitator 16 being refilled. In column 20, the BTX is withdrawn as overhead vapor through line 21. Residue is removed through line 22 and the BTX is introduced into distillation column 23. In this column benzene is separated from the remainder of the BTX and leaves the column as refined benzene at line 24. The remaining liquid toluene and xylene are withdrawn from the column by way of line 25, and sent to fractionating column 26. In column 26 the toluene is first volatilized and removed as overhead vapor by way of line 28 and valve 29. Xylene is then distilled off by way of line 28 and valve 29. Toluene and xylene are sent to storage by way of lines 33 and 33' respectively. Residue in column 26 is removed at line 27.

If desired, oleum may be used in the acid washing step at agitator 16, in place of concentrated sulfuric acid. Oleum will effect a more efficient removal of the thiophene from the BTX at this point, but with some small loss of benzene.

To obtain a benzene product low enough in thiophene to meet any and all specifications for commercial use, the benzene withdrawn from still 23 should be given an oleum wash, in addition to the wash at 16. Sulfuric acid of 66° Bé gravity may be substituted for the oleum in the wash at this point, but removal of the thiophene will not be as efficient. The oleum washed benzene will have a freeze point above 5.3° C, and, under efficient operating conditions, it is possible to obtain a benzene product having a freeze point as high as 5.45° C. The thiophene in the benzene treated with concentrated sulfuric acid would probably be no higher than 300 p.p.m. Benzene which has been oleum washed will have a thiophene content of about 0.5 p.p.m. or less.

The polyoxyalkylene glycol monoether absorbed used for scrubbing must be in the liquid condition at the point of use. These liquid glycol ethers have viscosities between 55 and 300 S.U.S. at 100° F, and have no substantial fractions boiling below 230° C. Certain glycol monoethers which fall within this group, can be ascertained and identified by reference to Union Carbide Chemicals Catalog No. F-6500G, entitled "Ucon Fluids and Lubricants," at page 24 (1960). The compounds are designated as Ucons in the catalog, and range from Ucon 50-HB-55 to Ucon 50-HB-300. The digits following the word "Ucon," the S.U.S. viscosity at 100° F. The molecular weight of these compounds will range between 250 and 2000. It has also been found that the glycol monoothers, or Ucons, described, mixed with the proper quantity of water (1 to 10 weight percent), can be used efficiently as scrubbing agents when diluted with up to as much as 25% by weight of diethylene glycol.

In the scrubbing operation, single or multiple units may be used, depending on the capacity required to scrub the existing gas volume. Units may be inserted in parallel, series, or parallel-series combinations to suit the requirements of individual plants. The individual units themselves may vary in operational details, and useful types include venturi scrubbers, unpacked spray towers, or with without recirculation, packed and packed-spray combination towers, and tray columns. In practice, the loose packings are usually metal turnings, and the trays are wooden grids (hurdles). The absorption efficiency of the scrubbing operation will be affected to some extent by the type of scrubbing medium used. However, the variations in absorption efficiency as between the different types of conventional scrubbing units is not great, and the type of scrubber selected will generally be a factor of availability and individual choice on the part of the operator.

In order to establish, clearly, the advantages of our scrubbing process, in terms of refined product, over prior conventional scrubbing procedure, two tests were made, each with a different scrubbing medium. In test A, the
The coke oven gas used in the tests had a proximate analysis, based on analyses made at times prior to, and subsequent to, the test runs, as follows:

**TABLE III**

<table>
<thead>
<tr>
<th>Components</th>
<th>Percent by vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>30.5±2.5</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2.3±0.3</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td>Propene</td>
<td>0.3±0.05</td>
</tr>
<tr>
<td>Butenes</td>
<td>0.07±0.02</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.02±0.002</td>
</tr>
<tr>
<td>Cyclopentane and/or</td>
<td>0.01±0.001</td>
</tr>
<tr>
<td>Pentanes or cyclopentanes</td>
<td>0.01±0.001</td>
</tr>
<tr>
<td>Methyl cyclopentane</td>
<td>0.01±0.005</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.01±0.005</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.5±0.10</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.2±0.05</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.05±0.001</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.1±4.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.9±1.0</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>6.1±1.5</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2.4±1.0</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>0.5±0.02</td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>0.01±0.002</td>
</tr>
</tbody>
</table>

Referring to FIG. 2, scrubber A, a five gallon counter-current, gas-liquid absorber, or scrubber, shown at 39, was charged with 8000 grams of the hydrocarbon wash oil. The scrubber was sealed and connected to the coke oven gas main by way of plastic tubing 37 and a % inch (i.d.) copper tube 34. Scrubber B, shown at 39', was charged with 7760 grams of the glycol monooether and 240 grams of distilled water. This scrubber was also sealed and connected to the gas main through plastic tubing 37' and copper tubing 34. In order to provide uniform, relative temperature in the absorption reactions during the entire test period, scrubbers A and B were maintained immersed in water baths 38 and 38', respectively.

At the start of the test, stopcocks 41 and 41' were opened, and coke oven gas was introduced into the system by way of copper tube 34. Part of the tubing, in coiled form, was surrounded by a water bath 35 to control the temperature of the incoming gas. The copper tubing led from the water bath to a moisture trap 42 containing glass wool. The coke oven gas, leading from the trap, entered plastic hose 36. This hose had a Y-joint leading to branches 37 and 37'. By means of the branched inlet tubes, it was possible to permit equal quantities of the gas to flow through each scrubber simultaneously, and to thus produce identically controlled operating conditions. As shown in Table II, these conditions were checked routinely during the test run. The gas exhausting from each absorber was metered on wet test gas volume meters 40 and 40'.

Exactly 300 cu. ft. of gas were passed through each absorber, in a period of 55 hours. At the end of the test, absorber A had an increase in weight of 132.5 grams. Absorber B had increased in weight by 192.5 grams. At the end of the run, the liquid absorbent and absorbate were removed from each absorber. The liquid from absorber A was distilled to separate and recover the absorbed light oil, which oil contained predominantly aromatic hydrocarbons. The crude light oil from absorber A weighed 163.5 grams, equivalent to 1.71% by weight of the original absorbent. About 50 ml of a black, gummy, tarry waste material settled out of the wash oil during and after the steam distillation.

The absorbent-absorbate from scrubber B was also distilled to separate the light oil therefrom. The crude light oil in this instance amounted to 128.1 grams, or 1.60% by weight of the original absorbent. There was no observation of any gummy, tarry material settling out from the absorbent of absorber B, either during or after distillation.

The light oils from the two absorbers were refined separately by the following steps:
1. Fractional distillation of the crude benzene-toluene-xylene (BTX) by distillation.
2. Acid washing of the BTX fraction.
3. Fractional distillation of the acid washed BTX to obtain purified benzene and toluene.

In the first refining step, 125.0 grams of light oil from absorber A were distilled to remove the forerunnings. Likewise, 121.9 grams of light oil from absorber B were distilled. The results of these distillations are shown in Table IV.
The residues from step 1 will contain from about 25% to 30% by weight of absorbent. The recovered BTX fractions from each absorber were acid washed separately with 66° Bé. sulfuric acid and neutralized with 18% sodium hydroxide. The washing procedure was performed by agitating 75. g. of BTX, in the case of absorber A material, and 75.0 g. in the case of absorber B material, in a 100 ml. separatory funnel with 1.5 ml. of the acid for 20 minutes. The agitated liquid was allowed to settle for 20 minutes, after which it was again agitated for 20 minutes, this time with a fresh 1.5 ml. portion of acid. After another 20 minute settling period, the samples were each agitated for 20 minutes with a 2.5 ml. portion of the caustic solution. This was followed by a 20 minute settling period, a second 20 minute neutralization with a fresh 2.5 ml. portion of caustic, and finally another 20 minute settling period. At the end of this procedure there remained 72.7 g. of washed BTX from absorber A and 70.2 g. of washed BTX from absorber B. Losses, represented by difference in weight between the washed BTX and the original BTX charged to the funnel before washing, include olefins and thiophenes.

In the third and final refining step, the washed BTX from each absorber was separately subjected to a fractional distillation. Results of the distillations are shown in the following table.

As can be ascertained from the table, only the benzene and toluene were volatilized in the distillations, the temperature being purposely held below the point at which xylene would distill over. This was done because of the extra operational precautions required to obtain xylene along with the benzene and toluene fractions, and the lack of significance of fractionally distilled values for xylene had they been obtained. The percentage of the xylene fraction in each case was determined by measuring the volume of residue in the distilling flask.

The combined benzene from absorber A had a freeze point of 5.0° C. and contained 0.025% olefins, while the combined benzene from absorber B had a freeze point (dry) of 5.3° C. and contained 0.023% olefins.

The combined distilled benzene from absorber A and the combined distilled benzene from absorber B were separately analyzed by gas chromatography. The resultant data are shown in Table VI, showing a reduction in aliphatic and aromatic contaminants in the case of absorber B, clearly demonstrating the advantage of the polyoxyalkylene glycol monooctyl-water absorbent over the conventional hydrocarbon oil.

Our invention provides a method by which coke oven plant operators are enabled to upgrade their benzene product with existing equipment.

This invention can also be practiced in conjunction with hydrogenation processes for refining benzene, by eliminating the acid or oleum washing treatment and feeding the forerun-free BTX to a hydrogenation reactor. For example, the glycol scrubbing step may precede a hydrogenation process, such as that described in U.S. Patent No. 3,081,259 to Donovan et al. By this mode of operation, the BTX product introduced into the hydrogenation reactor will be quite low in aliphatic compounds, thus reducing the hydrogen and thermal cracking requirements over those required for hydrogenating the BTX product resulting from prior scrubbing practices.

We claim:

1. A method of treating coke oven gas to recover a benzene product having a high freeze point which comprises scrubbing coke oven gas with an aqueous solution of a glycol of the type designated as polyoxyalkylene glycol terminal monoether having a gram molecular weight of about 250 to 1000 at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g. and thereby removing a liquid product of benzene, toluene and xylene from the gas with said solution, and separating benzene from the other constituents of the liquid.

2. A method of treating coke oven gas to recover a benzene product having a high freeze point which comprises scrubbing coke oven gas with an aqueous solution of a glycol of the type designated as polyoxyethylene-polyoxypropylene glycol terminal monoether having a gram molecular weight of from 250 to 1000 at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g. and thereby removing a liquid product containing benzene, toluene and xylene from the gas with said solution, separating benzene from the other constituents of the liquid.
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9 constituents of the liquid and washing the separated benzene with acid.

3. A method according to claim 2 wherein the separated benzene is washed with sulfuric acid.

4. A method of treating coke oven gas to recover a benzene product having a freezing point of 5°-5.2° C. which comprises scrubbing coke oven gas with an aqueous solution of a glycol of the type designated as polyoxyalkylene glycol terminal monoether having a gram molecular weight of from about 250 to 1000, said solution comprising water in an amount of from 1% to 10% by weight of said monoether at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g. and thereby removing a liquid product containing benzene, toluene and xylene from the gas with said solution, separating benzene from the other constituents of the liquid and washing the separated benzene with oleum.

5. The improvement in a method of treating coke oven gas to recover a benzene product having a high freezing point which comprises scrubbing coke oven gas with a liquid glycol of the type designated as polyoxyethylene-polyoxypropylene glycol terminal monoether having a gram molecular weight of from about 250 to 1000 and water in an amount of from 1% to 10% by weight of said monoether at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g.

6. The improvement in a method of treating coke oven gas to recover a benzene product having a freezing point above 5° C. which comprises scrubbing coke oven gas with an aqueous solution of a glycol of the type designated as polyoxyethylene-polyoxypropylene glycol terminal monoether having a gram molecular weight of from about 250 to 1000, said solution comprising water in an amount of from 1% to 10% by weight of said monoether, at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g.

7. The method of claim 3 in which from 1% to 10% water by weight is mixed with the glycol.

8. The improvement in a method of treating coke oven gas to recover a benzene product having a freezing point above 5° C. which comprises scrubbing coke oven gas with an aqueous solution of a polyoxyalkylene glycol terminal monoether having a gram molecular weight of from about 250 to 1000 having the following general formula

$$\text{HO} (\text{CH}_2\text{CH}_2\text{O})_x (\text{CH}_2\text{CH}_{\text{CH}_3})_y \text{C}_n\text{H}_{2n+1}$$

where x and y components occur in about equal molar concentration and n is an integer of from 1 to 5, said solution comprising water in an amount of from 1% to 10% by weight of said monoether at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g.

9. The improvement in a method of treating coke oven gas to recover a benzene product having a freezing point above 5° C. which comprises scrubbing coke oven gas with an aqueous solution of a polyoxyethylene-polyoxypropylene glycol terminal monoether having a gram molecular weight of from about 250 to 1000 and a Saybolt Universal viscosity of between 55 and 300 at 100° F., said solution comprising water in an amount of from 1% to 10% by weight of said monoether at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g.

10. The improvement in a method of treating coke oven gas to recover a benzene product having a freezing point above 5° C. which comprises scrubbing coke oven gas with an aqueous solution of the butoxy form of a polyoxyethylene-polyoxypropylene glycol monoether having a gram molecular weight of from about 250 to 1000, said solution comprising water in an amount of from 1% to 10% by weight of said monoether, at a temperature of from 20° F. to 120° F. and at a pressure of not more than 25 p.s.i.g.

References Cited by the Examiner

UNITED STATES PATENTS

2,730,558 1/1956 Gerhold 60-674
2,834,820 5/1958 Bloch 60-674

FOREIGN PATENTS

460,633 10/1949 Canada
11,758 11/1913 Great Britain

DELBERT E. Gantz, Primary Examiner.

C. E. SPRESSER, Jr., Assistant Examiner.