

ITEM II - ANALYTICAL METHODS

SUMMARY REPORT

The material in this Item is derived from the same source as Item I, Gelsenberg Benzine, Inc., but from a file covering a later period.

Sub-Items 1, 1a, 1b, 2, 2a, 3, 4, 5 and 6 deal with analysis and inspection of coal, for the most part by microscopic techniques. The reviewers did not feel competent to judge the value of this information to the by-product coal industry, but have labeled it as being of no value to petroleum company laboratories. The U. S. Bureau of Mines may be interested in seeing this material.

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ABSTRACTS AND TRANSLATIONS

7. Patent Application: Continuous Measurement of Aliphatic Hydrocarbons and Oxygen Compounds with Urea (Translation)

SECRET

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3. The receiver is responsible for its safe keeping under lock and key.

DISCOVERER  
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Frankfurt am Main

O.Z. 12 438.

B 190 197 IVa/12 O, Submitted March 18, 1940.

"Method for Separation of Aliphatic Oxygen-Containing Compounds and of Straight Chain Hydrocarbons of at Least 6 Carbon Atoms from Mixtures Containing Them.

"The method is based on the knowledge that aliphatic oxygen containing compounds and straight chain hydrocarbons combine readily with urea to form well defined and well crystalizable adducts whereas branched hydrocarbons are indifferent to this treatment. A minimum chain length of 6 carbon atoms is a prerequisite to the reaction.

"The adducts so obtained may be separated into their components by heating or by addition of urea-solvents, as for instance methanol and other lower aliphatic alcohols, but most readily by water or aqueous solutions. By using water one generally obtains a prompt separation of an aqueous solution of urea from the pure oxygen containing compound or hydrocarbon that forms the upper layer.

"This knowledge, then, is the basis of the present invention according to which one may separate aliphatic oxygen-containing compounds or straight chain hydrocarbons from mixtures containing them by adding urea, separating the adducts formed by decantation, filtration or similar means, and then decomposing the adducts into their components by heating or by addition of urea-solvents.

"Oxygen-containing compounds found to be separable from mixtures are for instance:

Octanol, primary and secondary	Caproic acid
Cetyl alcohol	Caprylic acid
n-Decyl alcohol	Undecylenic acid
Heptylaldehyde	Oleic acid
Nonylaldehyde	Palmitic acid
Decylaldehyde	Stearic acid
Undecylaldehyde	Pelargonic ester
Methyl-Nonyl ketone	Oenanthic ester
Methyl-Undecyl ketone	

"To apply the proposed process, one may bring any mixture containing the materials mentioned together with a concentrated solution of urea in water, methanol, or ethanol, and the like. The solid crystalline adducts will then separate out; thorough mixing will enhance the reaction. The adduct is separated and split into its components upon addition of water or aqueous solutions.

"In this way one may isolate higher alcohols such as are encountered in the crude state in the products of catalytic processes or fermentation processes.

"The method is, moreover, suitable for the decomposition of essential oils. Thus methyl-nonylketone may be separated from rue oil.

"The compounds which urea forms with higher alcohols, aldehydes, ketones, acids, and esters by the present method are presumably molecular compounds. In any case, the analysis in most instances has shown the composition to correspond to a complex of 6 urea molecules and 1 molecule of the other component.

"The formation of these compounds may in many cases already be observed under the microscope with the smallest of quantities. Thus by placing a drop of octanol on a hollow ground slide and adding some tiny urea crystals, one may in a few moments observe long fine needles shooting out between the comparatively coarse urea crystals. After a few minutes the urea crystals are covered by numberless fine needles suggestive of a magnet covered with iron filings. The rate of formation of these adducts varies with the materials. In the case of the esters I investigated, the rate of formation is so great that it is difficult to get the preparation under the microscope fast enough to recognize the urea crystals; they are completely overgrown. An equally attractive observation is the instantaneous formation of long fine needles of adduct at the surface of contact when a trace of the above-mentioned materials, such as pelargonic ester, is added carefully to a concentrated alcoholic solution of urea.

"Another important aspect of the present discovery is the separation of straight-from branched chained hydrocarbons in mixtures of hydrocarbons. This separation is of particular technical interest because the branched chain hydrocarbons, owing to their antiknock value make ideal fuels for gas carburetor engine motors, such as aviation motors. The straight chain hydrocarbons, on the other hand, owing to their ignition quality are preferred for diesel motors.

"The method is also of importance in the production of lubricating oils since the straight chain components generally have properties which are desirable from a lubricating point of view. It has been found that hydrocarbon mixtures of all kinds may be processed in the manner described. As starting materials the following may be mentioned: Mineral oils or their fractions, that is, gasoline, kerosene, gas oil, diesel oil, paraffin oil and vaselines. Further, hydrocarbon mixtures obtained by dry distillation of brown-coal or of hard-coal, as well as products of destructive hydrogenation of brown-coal, mineral oils and tar, and polymerized gasolines, cracked gasolines and similar compounds.

"In processing these materials according to the present method, one may treat them with a saturated solution of urea in methanol. The straight chain compounds then precipitate in the form of adducts with urea from which they are liberated through decomposition by heat or by addition of small amounts of water. The unreacted hydrocarbons, consisting essentially of branched chain compounds, may upon separation be used directly as fuels (aviation gasoline) of high antiknock value.

"Further experiments have shown that the amount of solvent used may be considerably reduced. It is only necessary to add sufficient solvent to completely wet the urea. In this way the small amount of the urea dissolved will separate in the form of adduct so that urea will again dissolve and react. Thus, one might say that the solvent acts as a catalyst.

#### Example 1

"50 g. ruc oil is thoroughly shaken with 500 ml. of a saturated aqueous or alcoholic solution of urea. The resulting crystalline paste is filtered dry by suction and decomposed by shaking with 200 ml. of water, whereby the methylnonyl-ketone separates from the aqueous urea solution.

#### Example 2

"A saturated solution of urea in methanol or ethanol will at once upon shaking produce a crystalline adduct with a drop of n-octane, but not with iso-octane. If the concentration of the urea is now reduced, the adduct is decomposed into its components. True to the nature of such empirical compounds, one might say that the adduct is stable only in an "atmosphere of urea". It decomposes spontaneously with water and yields unaltered n-octane. Similarly it dissociates upon dry heating to yield n-octane.

Example 3

Kerosene or gasoline is shaken with an excess of urea dissolved in methanol or ethanol. The resulting adduct is filtered by suction and then heated or treated with alcohol or water for separation of the normal hydrocarbons. The branched chain hydrocarbons are separated from the filtrate upon addition of water if necessary after removal of the main part of the solvent.

Example 4

100 ml. test gasoline (150-180°C) is stirred well with 40 g. of urea previously well moistened with about 35 ml. of methanol. Separation of the adduct is accomplished after a short time. As in Example 3, the latter is filtered off by suction and decomposed. Thus one obtains, as an example, about 40% normal- and about 60% iso-hydrocarbons.

Example 5

300 ml. paraffin oil is well shaken or mechanically stirred with 150 ml. of an alcoholic solution of urea. The separated crystals are washed with a fat-solvent. Splitting with water then yields the normal hydrocarbons in the form of soft wax. The splitting of this crystalline adduct with water is especially beautiful to watch. Under the microscope one may see how the small coarse crystals when wetted with a trace of water fly apart almost explosively to be replaced by numberless tiny oil droplets.

Example 6

Normal- and iso-hydrocarbons are also successfully separated from crude oils; in fact the method is particularly useful in this case. On shaking crude oil with an alcoholic solution of urea, 3 different portions are obtained. The normal hydrocarbons present separate out as a granular mass, carrying the tary constituents with it. Both may be separated by filtering under suction until dry because the tar is carried with the solvent into the filtrate and may be siphoned off as it is insoluble in the solvent. Or also: One filters by gentle suction allowing only the alcoholic solution to pass, and then after changing receiver applying strong suction to pass the tar. The last of the tar is removed by means of a suitable solvent. The iso-hydrocarbons are isolated from the alcoholic filtrate in the manner described above. Thus the crude oil has been separated into 3 different groups of components, namely 1) n-hydrocarbons, 2) tary components and 3) iso-hydrocarbons.

"This method might therefore be advantageous not only for purification but also in scientific investigation of crude oils.

Patent Claims

"1) Method for separation of oxygen-containing aliphatic compounds or of straight chain hydrocarbons from mixtures containing such, characterized by adding urea to these mixtures, separating the compounds formed by decantation, filtration or similar means, and isolating the pure compounds therefrom by application of heat or by addition of urea-solvents.

"2) Method according to claim 1 for separation of alcohols, aldehydes, ketones, esters or acids of the aliphatic series with at least 6 carbon-atoms, characterized by bringing mixtures containing them into reaction with urea, preferably in the presence of limited amounts of urea-solvents such as water or lower aliphatic alcohols, separating the adducts formed from the liquid, and liberating the above mentioned oxygen-containing compounds from the adducts by further addition of urea-solvents.

"3) Method according to claim 1, characterized by bringing mixtures containing straight chain hydrocarbons of at least 6 carbon atoms into reaction with urea, preferably in the presence of limited amounts of urea-solvents, separating the solids formed from the liquid parts and, finally, liberating the straight chain hydrocarbons by addition of more urea-solvents.

"4) Method according to claims 1 and 3, characterized by separating hydrocarbon-containing fuels via the urea-compound, into a part rich in branched chain hydrocarbons, (hence of high antiknock value) and a part rich in straight chain hydrocarbons suitable as diesel oil.

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8. Patent Application: Continuous Measurement and Recording of Boiling Point and Gravity During Distillation at Constant Heat Input (pneumatic-hydraulic with photoelectric drive) (Translation)

"January 3, 1944  
I. G. Farbenindustrie, AG.

Hersoburg

Our Number: OZ 14527 We/H<sup>6</sup>  
Ludwigshafen A/R., Dec. 23, 1943

"Apparatus for the Recording of Boiling Point Curves

In the manufacture and refining of petroleum, especially gasoline, and liquefied hydrocarbon gases, the most common test of the products is the construction of boiling point curves. The so-called Engler distillation test is most commonly used for this purpose. In this method a known quantity of gasoline in a distilling flask is evaporated by heating with a gas flame.

The vapors are condensed in a water-cooled condenser and the liquid collected in a graduated cylinder. The temperature is measured by means of a mercurial thermometer fitted in the neck of the distilling flask. The temperature and the quantity of distillate collected in the cylinder are read in definite time intervals and tabulated. The boiling point curve can then be constructed from the tabulated data. In performing the test it is especially important that the evaporation of the liquid in the flask takes place at a steady rate. Usually the number of drops falling in the graduate per unit time is counted to determine the rate, and the gas flame is regulated so it stays essentially constant.

"However, even with well-trained operators, the use of a condenser causes an unavoidable lag between the temperature and volume measurements, which can often lead to mistakes. Furthermore, a portion of the evaporated gasoline is not condensed with water cooling so that a so-called "distillation loss" occurs. All these shortcomings are avoided in the following invention, with which it is possible not only to read the separate measurements but also automatically to record them on a diagram.

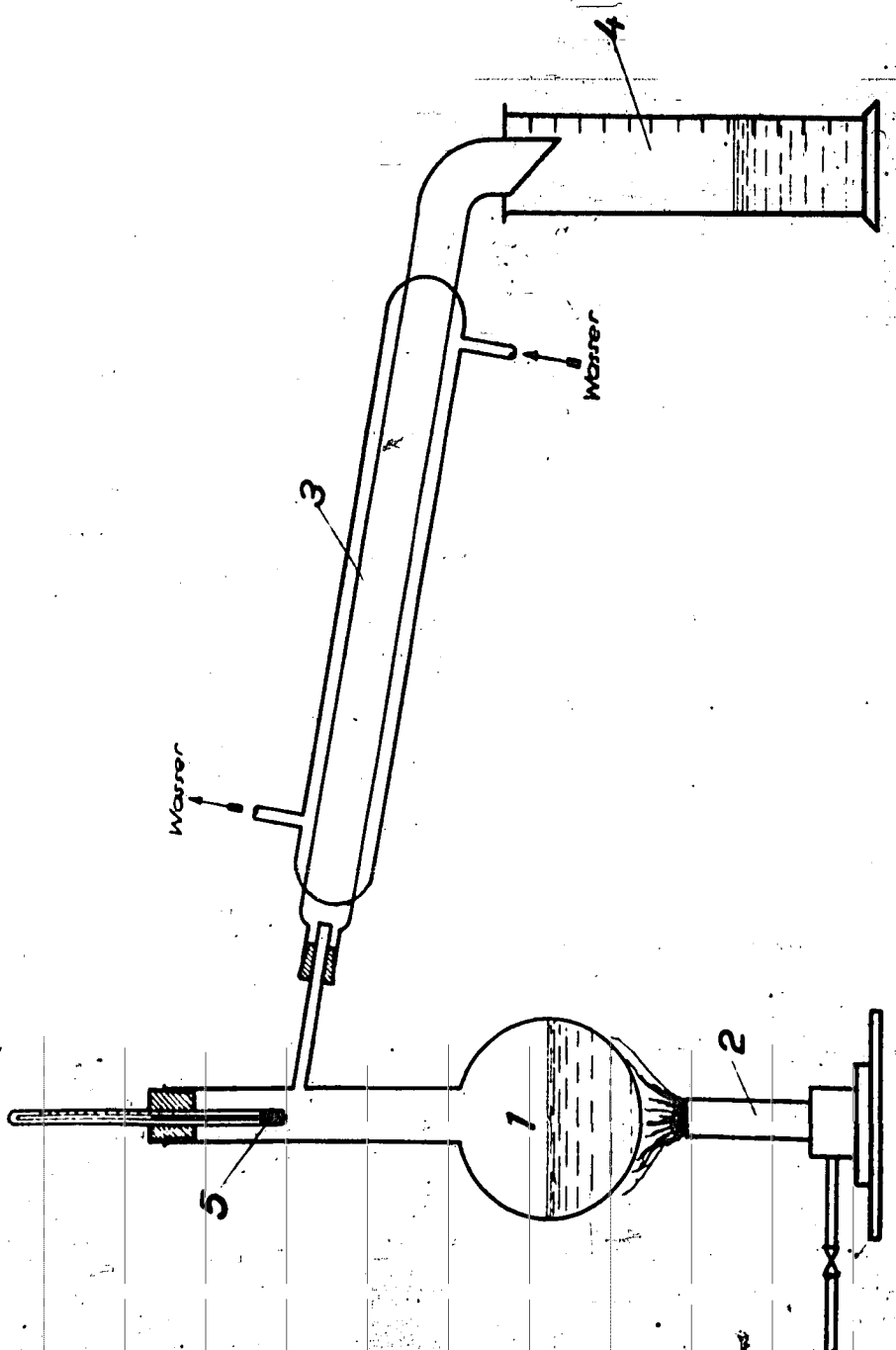
"The main feature of the invention is the immediate recording of the weight of the evaporated liquid during the distillation. Referring to Figure 1, the distillation flask 1, which has been fitted with an electric heater 2, is placed on a balance pan 3. The balance beam 4 carries a buoyancy bar 5 (aluminum). The latter dips in a pneumatically controlled compensating liquid contained in tube 6. The height of the liquid in tube 6 is governed by the pressure "P" above the liquid in reservoir 7. This pressure is due to the air or gas flow "Q" entering through valve 8, the exhaust of which is controlled by the nozzle 9 and pressure plate 10. The operation of the apparatus is as follows:

"After the electric heater is turned on, the liquid in flask 1 starts to boil. The evaporated liquid leaves the flask through the open side arm and can be removed by suction if necessary. Because of the evaporation of the liquid the weight of the liquid remaining in the flask is decreased and the pressure plate 10 begins to oppose, with slowly increasing power, the air which is flowing through the nozzle 9. This increases the pressure "P" in reservoir 7 and the compensating liquid in tube 6 begins to rise. The rise of the liquid level in tube 6 increases the buoyancy of the bar 5, and the equilibrium of the balance is restored. The liquid level in tube 6, and also the pressure "P" in reservoir 7, are therefore strictly proportional to the weight of evaporated gasoline "G". It is therefore easily possible, by means of the pressure measuring device 11, to indicate, or, as has been done here, to record, the weight of the evaporated gasoline. It is even possible to record the boiling point curve automatically, when the pen 12, is made to follow exactly the temperature of thermometer 13, in the distilling flask 1.

"Experience has shown that this can be done by using a photo-electrically controlled compensating device. In the case illustrated the pen 12, is connected with the core 14, of an induction transmitter. By means of a differential transformer 15, and the rectifiers 16 and 17, a difference potential "eg" is set up at the resistances 18 and 19, which is exactly linearly proportional to the position of the carriage 12.  
(Note by reviewer) 16 and 17 probably copper oxide rectifiers.

Figures 1 to 3 follow.

Fig. 1

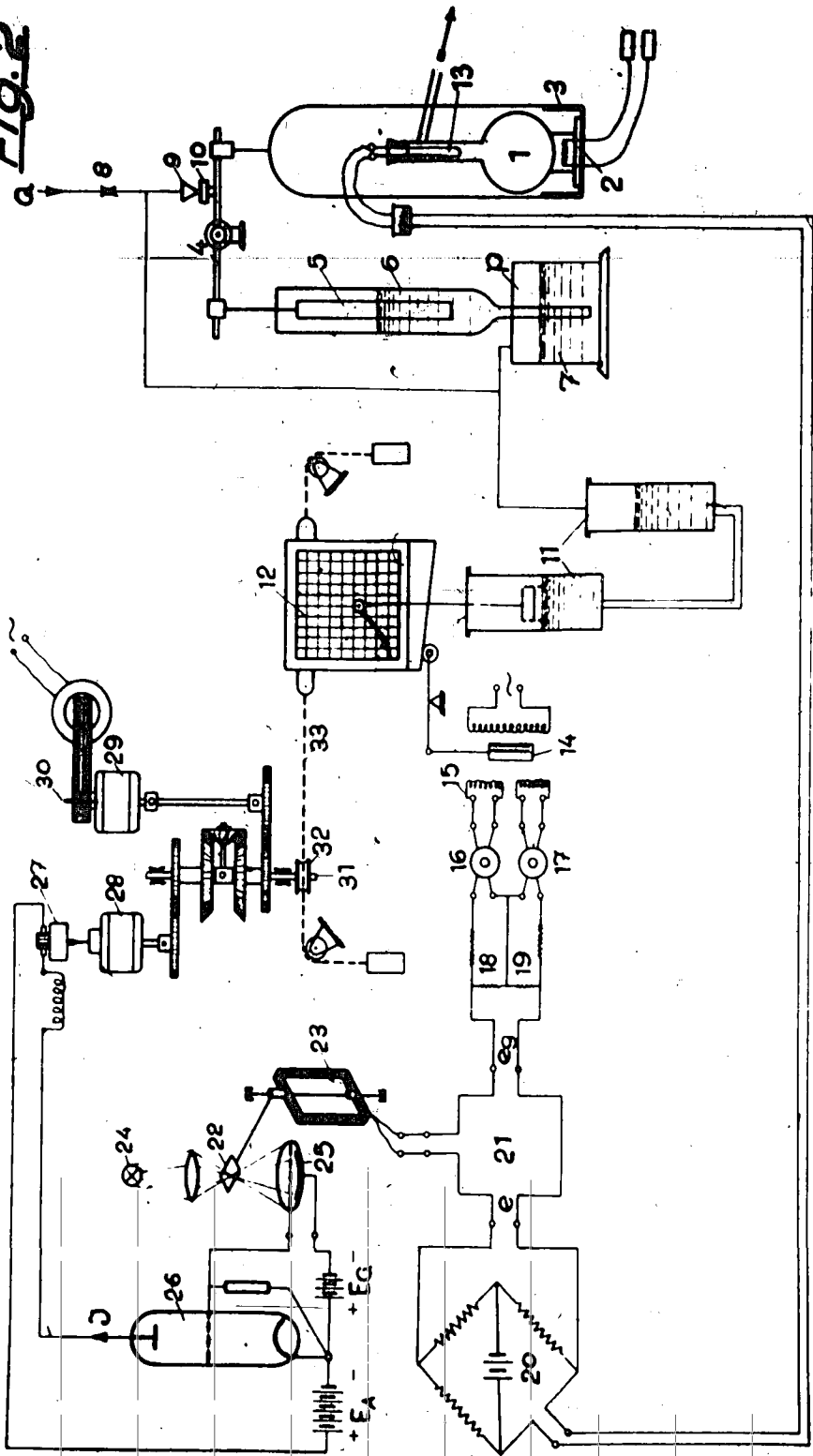


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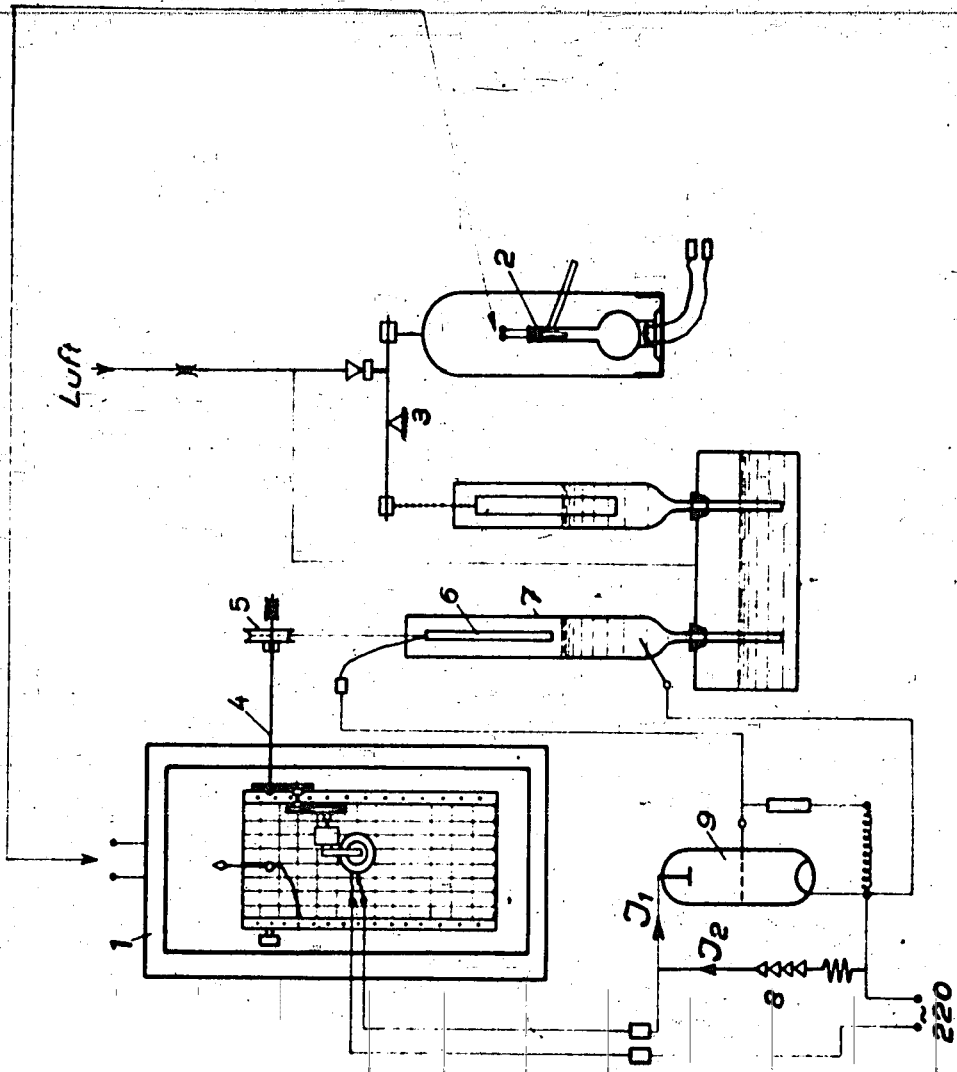
Fig. 2



Ammoniakwerk Merseburg G.m.b.H.  
 Betr. Kopfr. Nr. 26.10.1948 P.

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Fig. 3



Of course, the potential can also be produced by a resistance transmitter instead of an induction transmitter. The operation of the compensating device is as follows:

"With increasing temperature of the resistance thermometer 13, the potential "e" at the contact points of the measuring bridge 20 increases. As a consequence, the control potential "e" is greater than the compensating potential "eg", and a current flows in the control circuit 21, which causes the plate 22 of the nullgalvanometer 23 to move out of the light path of the bulb 24. Therefore the photocell 25 is illuminated more and more, and the anode current J of tube 26 decreases. This anode current J serves to control a collector motor 27. This motor turns by means of a pinion 28 one driving gear of a reversing gear assembly while the other driving wheel is turned through pinion 29 in the opposite direction by a synchronous motor 30 running at constant speed. The arrangement is set up so that, with a definite anode current, motor 27 has the same rpm. as motor 30. In this case the principal shaft 31 of the gear assembly is at rest. When, however, the anode current J increases above this nominal value, motor 27 runs faster; when J decreases, as indicated above, motor 27 runs slower and the main shaft 31 of the gear assembly moves the pen-carriage 12, by means of the sprocket 32 and chain 33, in the direction of increasing temperature. By the movement of the carriage 12, however, the potential "eg" is increased until "eg" is again equal to the control potential "e", finishing the compensating procedure.

"The chart carriage 12 is thus made to follow with great precision the potential "e" of the bridge 20, as well as the temperature of the thermometer 13. Therefore, the weight of evaporated liquid, as measured in manometer 11, is immediately recorded on the chart with the change in temperature. The device is therefore capable of recording the boiling point curves of liquids such as gasolines or liquefied gases. Furthermore, this apparatus has the advantage, as compared with present practices, that the recording of the boiling point curve is practically independent of the rate at which the liquid sample is evaporated, except that a definite maximum rate must not be exceeded. Thus it happens that the current of the electric heater 2 can remain constant throughout the whole evaporating procedure.

"With the construction explained above, it is possible to record the boiling point curves of any product with great accuracy and good reproducibility.

"If however, the size and form of the curve are not too important, experience has shown that the device can be simplified in such a way that the moving of the paper chart is not controlled by the temperature but by the weight of the evaporated gasoline. Such a construction of this invention has the great advantage that an ordinary temperature recorder (see Fig. 3) can be used to record the temperature of thermometer 2. The problem then becomes one of controlling the chart travel of the recorder by the pneumatic-hydraulic balance 5. This is done simply by installing a rope pulley on the shaft 4 (extended from the housing of recorder 1).

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"To the pulley is fastened a contact rod 6, which dips into the liquid level tube 7 of the pneumatic-hydraulic balance 3. For the control of the chart-drive motor of the recorder, the alternating current of the motor is divided into two half-waves by means of the one-way rectifier 8, and the amplifier tube 9. The amplifier is wired so that, when the contact rod 6, dips in the electrically conducting liquid of the tube 7, the negative potential is led off the grid so that an anode current  $J_1$  flows. This forms with the half-wave current  $J_2$  of the rectifier 8 a normal alternating current which turns the chart-drive motor of recorder 1, moving the paper, and, at the same time, raising the contact rod 6. As soon as the contact rod no longer dips in the liquid, the negative potential at the grid of tube 9 is re-established. The anode current  $J_1$  is discontinued and the chart-drive motor of recorder 1 is suddenly stopped by the half-wave direct current  $J_2$ . Since the opening and closing of the contact takes place in extraordinarily small steps (about 0.1 to 0.2 mm. in a total distance of 200 mm.) the paper will be moved practically continuously. To move the contact rod 6 back after finishing the experiment, the rope pulley is provided with a friction coupling.

"This manner of construction of the apparatus has the advantage (as compared to the method first described) that the rapid changes in chart-drive rate present at the start of boiling are avoided, because the evaporation of the liquid, and also the rise of the compensating liquid, takes place at a rate which changes but little.

"The apparatus and methods described serve a very good purpose, especially for the control of distillation equipment, because it is now possible to record boiling point curves automatically in the shortest possible time and without specially trained personnel.

#### "Patent Claims

- "1. Apparatus for the recording of boiling point curves of liquids or liquefied gases, in such a way that the weight of the liquid evaporated at constant heat input is measured or recorded continuously.
- "2. Apparatus, as in claim 1, in which is used a pneumatic-hydraulic balance for the measurement of the weight of evaporated liquid.
- "3. Apparatus, as in claims 1 and 2, in which is used a photoelectrically controlled compensating device for the movement of the chart with changes of the boiling point temperature.
- "4. Apparatus, as in claim 1 and 2, in which is used an ordinary temperature recorder, the chart-drive of which is controlled by the pneumatic-hydraulic balance.

I. G. Farbenindustrie"

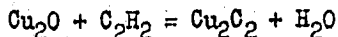
10. Determination of Small Amounts of Acetylenes and Hydrocarbons in Liquid Oxygen from a Linde Plant (Translation)

I. Determination of Acetylene

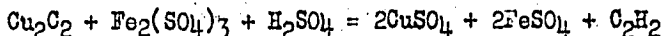
"1) Fundamental Considerations and Method.

The quantitative determination of acetylene in liquid oxygen in the main condensers of the air separation plants is carried out as follows:

The acetylene-containing oxygen from the main condensers is filled in 5 l. copper vessels (in the plant generally called copper cans). These are allowed to stand open for some time whereby the majority of the oxygen vaporizes into the atmosphere, while the total acetylene remains in the rest of the liquid oxygen. After this the copper can is closed and the vaporizing oxygen with the acetylene is passed through a series of wash bottles filled with ammoniacal copper salt solution, so-called Ilosvay's solution, (designated in the following as I-solution). The cuprous salt, prepared by reduction of cupric salt with hydroxylamine reacts with acetylene giving a cherry-red precipitate of cuprous acetylide, presumably according to the equation;



This precipitate is washed well and dissolved in a solution of ferric sulfate.



The formed ferrous sulfate is then determined with 0.01 N potassium permanganate solution. Since pro mol acetylene 2 ferrous ions are formed, 1 ml. 0.01 N  $\text{KMnO}_4$  solution corresponds to 0.13 mg. acetylene. The amount of acetylene found was originally present in 5 l. liquid oxygen.

The acetylene content in the liquid oxygen from the main condensers of all the Linde plants in Ludwigshafen should not exceed 2 mg./5 l. of liquid oxygen (see Paragraph 9 of the special directions for the nitrogen and oxygen plant). In the liquid separators of the Krypton enrichment columns, which are located in cellars between special protective walls, the acetylene content can increase to a maximum of 5 to 10 mg. per 5 l. liquid oxygen. Normally an acetylene determination should be made every 4 hours on each apparatus and, if necessary, within shorter time intervals.

"2) Procedure.

The 5 l. copper cans are cylindrical and have on top a conical opening which can be closed with a rubber stopper. They have a copper side tube which reaches almost to the bottom. Through the rubber stopper leads a glass tubing which connects the copper can with a pressure release vessel and from there with the gas washing bottles containing the I-solution. The filling of the cans on the apparatus has to be made in such a manner that

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the liquid oxygen is introduced rapidly until it overflows. In the spontaneous evaporation which with 5 l. liquid oxygen requires approximately one hour, the formed gaseous oxygen is released to the atmosphere as long as liquid oxygen comes out of the copper side tube when the can is closed momentarily. If this is no longer the case, the copper can is connected to the pressure release vessel (glass cylinder with glass tubing reaching almost to the bottom). The latter is filled with calcium chloride solution in order to prevent freezing. As long as excess pressure is maintained, it is released by the blow-off tube. As soon as the pressure decreases, the vaporized oxygen and acetylene is passed through the I-solution.

This solution is prepared freshly for each analysis by mixing the following solutions in the order named: 50 ml. of 10%  $\text{CuSO}_4$  solution (designated in the following as solution I), 20 ml. of 20%  $\text{NH}_3$  solution (designated as solution II), 100 ml. of 15%  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution (designated as solution III), 80 ml. of distilled water.

These 250 ml., distributed in five gas washing bottles, normally last for the determination of the acetylene content of five liters of liquid oxygen. The reagent should have a light blue color which darkens on shaking.

The cuprous acetylide which is formed is transferred quantitatively to a sintered glass Buchner funnel and is first washed with a 1.25% ammoniacal solution of hydroxylamine hydrochloride (wash solution) and then washed with distilled water until a portion of the filtrate will not discolor one drop of 0.01 N  $\text{KMnO}_4$  solution. Then the precipitate is dissolved in 20 ml. of  $\text{Fe}_2(\text{SO}_4)_3$  solution (called iron salt solution in the plant). This is done by adding the iron salt solution slowly to the precipitate on the filter crucible. After complete solution, suction is applied and the crucible is washed thoroughly. To the solution, phosphoric acid is added dropwise until complete decolorization. The solution is then titrated with 0.01 N  $\text{KMnO}_4$  solution.

Before evaluation of the analysis the titre of the iron salt solution must be determined because this solution invariably contains some ferrous salt.

### "3) Directions for the Preparation of Solutions.

It is advisable to prepare the following stock solutions for the acetylene determination: (1) Ten liters of I-solution, (2) five liters of iron salt solution, and (3) sixty liters of wash solution.

Solution I. 1000 g. of c.p. copper sulfate are dissolved in the cold in 10 liters of distilled water with shaking and filtered.

Solution II. Consists of 20% ammonia solution.

Solution III. To a large glass funnel containing a fluted filter paper are added 1500 g. of hydroxylamine hydrochloride. The salts dissolved by pouring cold distilled water through the filter. After the salt is completely dissolved, the solution is diluted to ten liters volume.

### Iron Salt Solution.

A round bottom flask of 5 liter capacity is filled half full with distilled water. Then 500 g. of  $\text{Fe}_2(\text{SO}_4)_3$  is mixed with 1000 g. of c.p.  $\text{H}_2\text{SO}_4$  in a 1 liter beaker. This mixture is added slowly with stirring to the water, the solution diluted to 5 liters, and filtered after mixing.

### Wash Solution.

In a 60 liter container, containing 750 g. of hydroxylamine hydrochloride, 12 liters of 20% ammonia water are added and the solution diluted to the 60 liter mark with distilled water.

### "4) Apparatus.

In a plant, having for example three air separation apparatus, and where two analyses per apparatus per shift are made, the following analytical equipment is required: a) Three to four copper cans of 5 liter capacity with side tubes leading nearly to the bottom and equipped with a rubber stopper at the neck of the cans. b) Two long-stemmed copper funnels of 15 cm. diameter for filling the cans with liquid oxygen. c) For each copper can a glass bottle of 5 liter capacity filled with water and having a siphon tube which can be connected by means of rubber tubing to the side tube of a copper can, in order to displace the residual gas in the can after vaporization is complete. It is advisable to arrange the glass bottles containing water on a rack above the copper cans. d) Three or four pressure release vessels to release the excess pressure of the vaporizing oxygen. These consist of narrow glass cylinders approximately 30 cm. in length and are equipped with two-holed rubber stoppers. One of the holes contains a glass T-connection, one arm of which connects by means of rubber tubing to a glass tube extending nearly to the bottom of cylinder. By means of a pinch clamp on the rubber tubing, this connecting can be closed off. The other opening in the rubber stopper serves as a pressure release. The two other arms of the T connect the copper can in series with the wash bottles. e) Approximately twenty gas washing bottles with good glass joints having inlet tubes reaching nearly to the bottom. For this determination, in each case, five bottles are connected in series with rubber tubing. f) A ten liter bottle with siphon for each of the following:

- 1) For copper solution (Solution I)
- 2) For the ammonia solution (Solution II)
- 3) For the hydroxylamine hydrochloride solution (Solution III)
- 4) For the wash solution
- 5) Storage for distilled water.

Each siphon is held in the bottle by means of a rubber stopper, and extends to the bottom of the bottle and has a short piece of rubber tubing at the outlet end on which a pinch clamp may be placed. It is recommended that the distilled water and wash solution be piped to the work bench. g) A good working aspirator for filtering the precipitate by vacuum. h) Three sintered glass Buchner funnels (porosity G-2, 40, 60, and 90 mm. diameter, respectively) and a filter flask. Filter paper disks fluted filter paper.

1) Titration stand with two liter reagent bottles,

- 1) For the iron salt solution,
- 2) For the  $KMnO_4$  solution,

which are connected to burets. Finally a bottle containing concentrated phosphoric acid. k) A few policemen to remove the copper precipitate from the gas wash bottles, several test tubes, rubber stoppers and rubber tubing.

#### "5) Special Directions.

Because of the extreme importance of the determination of the acetylene content of liquid oxygen and because of the small amount to be analyzed, it is evident that the operators engaged in these analyses exercise extreme care and cleanliness. In addition cleanliness is of prime importance because careless work may cause injury of the skin due to the corrosive action of the hydroxylamine solution. Gloves with leather gauntlets should be worn by the operator while working with hydroxylamine hydrochloride solutions. In order to obtain results of maximum accuracy, the following points should be observed:

a) The filling of the copper cans on the apparatus has to be done in such a manner that the oxygen is filled to overflowing as rapidly as possible. It is essential that the can is filled in one operation without making additions. During this operation goggles and canvas gloves should be worn.

b) The copper cans should be connected to the absorbers containing the I-solution when the liquid oxygen level is such that a small amount of liquid will evaporate through the pressure release vessel. As soon as the excess pressure is released, the rubber tubing connecting to the pressure release vessel is clamped shut so that the gas will pass through the I-solution. As soon as the gas stream, passing through the I-solution, has nearly stopped the residual oxygen in the copper cans is displaced by water. It is essential that in this operation no water enters the wash bottles. When the analysis is complete, the copper cans must be thoroughly dried so that no plugging from ice formation will take place in subsequent analyses. It is advisable to check the seams of the copper cans once each week for leaks.

c) The I-solution should always be freshly prepared. This reagent should have a light blue color which darkens on shaking,

d) The size of the Buchner funnel is determined by the amount of precipitate. Therefore funnels of 40, 65, and 90 mm. diameter should be available. During filtration care should be taken that the precipitate is transferred quantitatively to the filter. Precipitate adhering to the wash bottles should be transferred by means of a rubber policeman. At no time should the copper acetylide precipitate or any part of it be allowed



to become dry. The washing of the precipitate is continued until a portion of the filtrate will not decolorize a drop of potassium permanganate solution. The fritted glass filters are cleaned with c.p. hydrochloric acid solution. Blank determinations should be made by each shift to determine the titre of the iron salt solution as follows:

Approximately 25 ml. of the I-solution are filtered through a clean filter and the filtrate treated in the same manner as during an analysis. The consumption of permanganate by the blank solution, which should not exceed 1 ml. per ml. of iron salt solution, is then deducted from the volume obtained during analysis.

Example

KMnO <sub>4</sub> solution consumed	2.6 ml.
Blank for 25 ml. of iron solution	<u>0.6</u>
Actual consumption	2.0 ml.

$$2.0 \times 0.13 = 0.26 \text{ mg. acetylene per 5 liters of liquid oxygen.}$$

II. Determination of Hydrocarbons in Liquid Oxygen.

"1) Fundamental Considerations and Method.

The control of the hydrocarbon content of liquid oxygen in the main condensers of the air separation plants is carried out as follows:

One hundred ml. of the oxygen to be analyzed is placed in an unsilvered dewar. From the dewar it is slowly evaporated, and the resulting gas is passed through potassium hydroxide and barium hydroxide solution to remove any carbon dioxide, the purified gas in turn being passed over hot copper oxide. Hydrocarbons present are oxidized to carbon dioxide which is collected in a known volume of barium hydroxide solution. The excess of barium hydroxide is back-titrated. The consumption of barium hydroxide is then a direct measure of the amount of hydrocarbon oxidized; one ml. of 0.1 N Ba(OH)<sub>2</sub> solution = 0.6 mg. C. The hydrocarbon content expressed as mg. C in the liquid oxygen from the main condensers of all air separation apparatus in Leuna should not exceed a maximum of 200 mg. per 5 liters of oxygen. The liquid separator of the krypton enrichment columns, which are located in the basement between special protective walls, the hydrocarbon content may reach a maximum of 500 to 800 mg. per 5 liters of oxygen.

Normally every eight hours an analysis should be made for each apparatus.

"2) Procedure.

From a larger quantity of liquid oxygen the volume of which should have been reduced as little as possible to prevent hydrocarbon enrichment, 100 ml. are transferred to a calibrated 100 ml. unsilvered dewar. The dewar flask is equipped with a two-hole rubber stopper.

Through one of the holes passes a glass tube which is connected to a nitrogen cylinder. Through a glass tube in the other hole of the rubber stopper the gas to be analyzed escapes and is passed through a spiral type gas washing bottle: one containing potassium hydroxide solution (1:3) and the other barium hydroxide solution. From here the gas is passed through a soda lime tower to remove any last traces of carbon dioxide. The gas from the soda lime tower is passed upward through an electric oven which contains a quartz tube packed with copper oxide (copper oxide wire). The oven is maintained at a temperature of 650° (23 mv. as measured with chrome, nickel -B- thermocouple). The carbon dioxide formed from the combustion is passed through several Meyer tubes arranged in series containing standardized barium hydroxide solution. After complete evaporation of liquid oxygen, which requires approximately 3 hours, the whole apparatus is purged for 15 minutes with pure nitrogen. The consumption of barium hydroxide is determined by titration with standard hydrochloric acid solution to the phenolphthalein end point. It is recommended that the titration is carried out at 0°C in an Erlenmeyer flask. During the titration a stream of nitrogen is passed over the solution being titrated to exclude carbon dioxide from the air. The nitrogen used must be scrubbed thoroughly to remove traces of carbon dioxide. The distilled water used should be freed of carbon dioxide by boiling and should be stored under a blanket of nitrogen.

#### Example

The Meyer tubes contain 150 ml. of 0.1 N barium hydroxide having a titre corresponding to;

149.2 ml. of 0.1 N hydrochloric acid solution. After completion of the analysis the titration corresponded to;

146.0 ml. of 0.1 N hydrochloric acid solution. The consumption for 100 ml. of liquid oxygen is therefore;

3.2 ml. of barium hydroxide solution.

Since one ml. of 0.1 N barium hydroxide is equivalent to 0.6 mg. of C the hydrocarbon content of 5 liters of oxygen is equal to;

$$0,6 \times 50 \times 3,2 = 96 \text{ mg. } C/5 \text{ liters of oxygen.}$$

#### "3) Apparatus

Requirements for one apparatus:

- a) One unsilvered devar flask of 250 ml. capacity with calibration mark at 100 ml. level, equipped with two-hole rubber stopper. One connection (rubber tubing) leading to nitrogen cylinder and the other to the carbon dioxide scrubbers. The latter consists;
- b) Two spiral type gas washing bottles filled with potassium hydroxide, one filled with KOH solution (1:3) the other filled with 0.1 N barium hydroxide solution. One drying tower filled with soda lime, washing bottles and tower arranged in series.

From the drying tower the connection leads to;

- c) Electric oven maintained at  $850^{\circ}\text{C} = 23$  mv. and, measured with chrome nickel - B - thermocouple. The copper oxide used, approximately 500 g., equal to 250 ml. (copper oxide wire), is contained in a quartz tube, one meter in length and 30 mm. in diameter, the upper and lower ends of which protrude from the furnace and are filled with porcelain chips.

From the oven the gas passes directly to;

- d) Two to 3 Meyer tubes containing each about 50 ml. of Standard barium hydroxide solution.

Further are required;

- e) An ice-cooled vessel in which the contents of the Meyer tubes are titrated.  
f) One five liter bottle for 0.1 N barium hydroxide solution, one five liter bottle for 0.1 N hydrochloric acid solution, one ten liter bottle for distilled water (carbon dioxide free), one dropping bottle containing phenolphthalein indicator solution.  
g) Nitrogen cylinder for purging the apparatus. The nitrogen before use is passed over hot copper oxide, washed and dried. For washing and drying of the nitrogen are required;  
2 spiral type washing bottles containing potassium hydroxide solution (1:3),  
1 spiral type washing bottle containing concentrated sulfuric acid, and  
1 drying tower filled with soda lime.

The electric oven mentioned under c) is capable of housing 4 quartz tubes so that only one oven is required for the control of 4 units.

#### "4) Special Directions.

a) In assembling the apparatus it is essential that the connecting lines consist of glass and short lengths of rubber tubing. The latter should never become brittle and should therefore be replaced frequently.

b) Before using the oven, the copper oxide should be heated at  $850^{\circ}\text{C}$  in a stream of nitrogen for 24 hours in order to remove any carbon dioxide or hydrocarbons. The complete removal of carbon dioxide is checked with barium hydroxide solution,

c) In order to protect the rubber connections close to the oven from the radiant heat of the oven, the rubber stoppers in the lower part of the quartz tubes are protected by asbestos shields. The upper part of the quartz tubes are constricted to about 8 mm. and bent in a right angle. There should be about 7 cm. beyond the bend which is then connected with rubber tubing to the Meyer tubes.

d) The prescribed temperature of  $850^{\circ}\text{C}$  should be maintained within close limits. It should not decrease, otherwise part of the methane in the oxygen will not burn completely. On the other hand the temperature should not be increased unduly because the copper oxide will sinter. Therefore, the temperature should be continuously controlled.

e) The barium hydroxide solution should be protected from the carbon dioxide of the air. This is done either by storage under an atmosphere of nitrogen or by attaching soda lime tubes to the bottle."

11. Concerning the Determination of (Free) Sulfur in Propane and Butanes (Translation)

"The values found by Benzol Association in our propane-butane are invariably lower than those determined by us (Gelsenberg Benzine, Inc.). This difference is caused by use of different analytical methods. The Benzol Association oxidizes the residue from the evaporation of propane-butane with aqua regia in reversed (umgekehrten) proportion, while in our laboratory, we oxidize the sulfur (elementary?) with bromine.

"Both oxidation methods were tested with pure sulfur flowers. It was found that the oxidation with aqua regia in reversed proportion takes place only very slowly. For the oxidation of only a few milligrams of sulfur, approximately 7 hours are required and even then  $KClO_3$  has to be added for more rapid oxidation, in order to obtain satisfactory results. In contrast, oxidation with bromine proceeds very rapidly. For complete oxidation, 1/2 hour is sufficient.

"In the following table (table missing), the analysis are summarized. In the oxidation with bromine, the values found by analysis agree well with the true sulfur content. In the oxidation with aqua regia and  $KClO_3$ , the agreement is not good. The values found are invariably lower than true. Therefore, it has to be considered that the oxidation with the reversely proportional aqua regia takes a very long time (7 hours) and that it is quite possible that, with less accurate and more rapid work, not all the sulfur is oxidized and much too low results are found. As it was in our case, it can happen that only 50% of the sulfur is recovered.

"To check our analysis, the bromine was tested for absence of sulfur. This was found to be the case. However, in the reagent used for the aqua regia -  $KClO_3$  mixture, rather high blanks were found. The amounts of sulfur in the reagents used are as follows:

20 ml. conc. HCl = 0.09 mg. S  
20 ml. conc.  $HNO_3$  = 0.15 mg. S  
3 g.  $KClO_3$  = 0.18 mg. S

Because of the low sulfur contents, the sulfur in the reagents is of great importance.

"It follows from this investigation, that the values obtained with bromine for the (elementary?) sulfur content of propane-butane are accurate. The oxidation with reversed proportioned aqua regia, when too rapid and not accurate analyses were made, will obtain low results."