# UNITED STATES PATENT OFFICE.

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## MOTOR-SPIRIT.

1,318,060. Specification of Letters Patent. Patented Oct. 7, 1919.

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*To all whom it may concern:*

Be it known that I, CARLETON ELLIS, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful improvements in Motor-Spirits, of which the following is a specification.

This invention relates to a petroleum product suitable for use in automobile engines and the like, and relates in particular to a motor spirit of gasolene-like material which may be obtained through the pyrogenetic decomposition or cracking of kerosene or heavier oils and other treatment as will be hereinafter illustratively described. This application is divided from my copending application Serial No. 785,855 renewed Serial No. 266,512.

In producing one form of the product comprised under the present invention I may start with a petroleum oil, say, kerosene, which may have a gravity of 42° Bé. or thereabout. This may be passed through a heated conduit, as for example, an iron pipe of a length preferably 50–100 feet, which pipe is preferably heated to around 425 to 480° C. and in some cases may be packed loosely with suitable contacting material such as nickel plated fragments of iron of irregular shape. Also in some cases water may be introduced with the kerosene or other oil, if desired, although tending to somewhat retard the splitting operation, but on the other hand, sometimes having a favorable influence on the character of the resulting product. Five per cent. of water calculated on the amount of oil introduced, is usually a satisfactory proportion. As stated, the use of water is optional.

The product emanating from the conduit forming the heating zone consists of fractions which on the one hand are lighter than the kerosene or the oil employed and on the other hand contain heavier products probably due to polymerization during the treatment. Very curiously these are oftentimes so proportioned that the specific gravity of the light oil counterbalances that of the heavier oil formed and the mixed distillate may thus show approximately the same specific gravity as the original kerosene or similar oil. For instance, a 42° gravity kerosene may give a product of almost precisely this gravity or perhaps 42.5 or 43° Bé. which may contain 30% or so of gasolene-like material.

The product obtained by this pyrogenetic treatment is separated into lighter and heavier parts by fractional condensation which may be followed, if desired, by fractional distillation and a gasolene fraction boiling to 125° C. or 150° C. obtained. This fraction is usually of brown color and of disagreeable odor.

When one attempts to refine it in the ordinary way using concentrated sulfuric acid followed by alkali, the gasolene tends to blacken or darken through formation of a relatively large amount of tar or coke-like material and this discoloration is not easily removed by water and alkali. In oil refining operations, so objectionable is the diluting effect of any water which may be present in the oil on the strong acid used that it has been recommended, for example, to very carefully dry the oil prior to the actual acid refining step. With cracked raw material of the present process this is not desirable unless, of course, excessive amounts of water be accidentally present. In the treatment of cracked gasolene, containing a substantial proportion of unsaturated bodies, I have found that acid which is more or less diluted with water acts more satisfactorily than the concentrated acid, which is contrary to expectations. Acid of 40–70% strength of sulfuric anhydrid causes a better and more satisfactory conversion of the unsaturated material.

An illustrative example will serve to make this clear. Kerosene of 42° Bé. was run through a tube of suitable length heated to such a temperature that the escaping oil vapors were maintained at a temperature about 465° C. which required a temperature about the tube of approximately 630° C. The vapors were passed through an air condenser then through a water condenser and finally the gases escaping from the latter were bubbled through heavy oil in order to remove some of the entrained condensable material. A portion of the condensate was distilled and cut at 105° C. and a fraction of gasolene-like material having a gravity of 55° B. was obtained which amounted to

25% of the total condensate taken for distillation. When the same condensate was cut at 140° C. instead of 105° C. the fraction obtained amounted to 27% and had a gravity of 54.5° B. Similarly when a third portion of the condensate was cut at 150° C. a fraction amounting to 32% of the original condensate was obtained and the gravity of this material was 53° B. The residue in the retort had a gravity of approximately 38° Bé. From the heavy washing oil through which the gases from the cracking stage were bubbled as described above a further yield of gasolene-like material was obtained.

The gravity of the product as drawn from the heated tube was 43° Bé, or only one degree lighter than the original kerosene. On exposing the fraction distilling over below 100° C. to air in an open dish, the major proportion of the material evaporated leaving a thick greasy material of whitish color resembling very soft vaseline. On very careful distillation of the crude gasolene or on passing air through the latter a similar product was formed which separated to some extent from the volatile hydrocarbons.

The thick greasy material referred to in the specific illustrative example set forth above, which may for convenience be called polymer "A," and which probably was a product of polymerization and oxidation, in the particular case noted above, decomposed when heated, vapor being given off at 110° C. and a transformation accompanied by a slight or mild explosion taking place at 125° C. This applies to the separated polymer "A," obtained as described, as in solution in the hydrocarbon, the heating may be carried up to 160° C. or so, without explosion, but usually with the disengagement of some gas. When polymer A is heated to 125° C. the reaction which takes place causes the formation of considerable gas and the production of a brownish liquid of somewhat thinner consistency than polymer "A."

A quantity of the crude spirit obtained in this illustrative manner and which distilled up to 150° C. in an ordinary distilling apparatus was fractionated with a rectifying column and the following fractions were obtained:

| Fractions. | Percentage by volume. | Iodin number |
|---|---|---|
| | *Per cent.* | |
| No. 1, up to 70° C. | 9 | 310 |
| No. 2, 70-85° C. | 8.4 | 233 |
| No. 3, 85-100° C. | 8.6 | 218 |
| No. 4, 100-115° C. | 9.2 | 168 |
| No. 5, 115-130° C. | 8 | 136 |
| No. 6, 130-150° C. | 14 | 87.8 |
| No. 7, above 150° C. | 19 | 53 |

The color of the different fractions above tabulated varied from practically colorless in number 1, nearly colorless in numbers 2 and 3, slightly darker in number 3 and 4, progressively to rather dark brown products in fractions 6 and 7. All the fractions ignited easily in an open dish at room temperature except fraction 7 which ignited but not as readily. When these fractions are burned in open dishes a resinous-like residue forms in some of them, the largest amount being present in fractions 2 and 3, boiling between 70 and 100° C. The formation of this resinous body may be ascribed to the presence of polymer "A" and may be eliminated by suitable hydrogenation, but with great difficulty by distillation.

The formation of these resinous or sticky materials in the carbureters of an internal combustion engine of course soon cause trouble.

When agitated with about 5% of sulfuric acid of 50% strength, the acid quickly turns a deep brown, but the motor spirit remains clear, or at the most is only tinted a yellow color. After agitation in this manner, the acid is removed by washing with water and, for example, about 5% of caustic soda solution of 20° Bé. is introduced and the hydrocarbon agitated for a time until reaction is complete; then the product is washed thoroughly with water to remove the alkali.

A quantity of this material passed through a carbureter which previously has been weighed was found to leave the apparatus free from resinous traces and any residue, if present, was negligible in amount.

The foregoing illustrates the results obtained with one sample of oil under certain conditions and, of course, considerable variations arise with changes in temperature, pressure and nature of the raw materials yielding a variety of products falling within the range of my invention.

The above mentioned residue left in the retort in the practice of the process and having a gravity of 38° Bé. when passed through a heated tube under approximately the same conditions, gave a yield of gasolene-like material of which 26%, or thereabout, was obtained by distilling up to 150° C. This is somewhat less than the percentage of gasolene-like material obtained from the first running using the original kerosene of 42° Bé., in which case over 30% of gasolene-like material distilling up to 150° C. was secured.

By the term gasolene-like material I do not wish it to be inferred that the product derived in this manner is exactly like gasolene chemically, because ordinary or natural gasolene is either entirely saturated or shows a very slight iodin absorption and may be refined with sulfuric acid of full strength. The iodin number of the raw or crude low-

boiling gasolene-like material obtained by this method before treatment with sulfuric acid may in some cases range around 100 to 150 and for certain fractions these may run much higher as indicated above.

Instead of using sulfuric acid under conditions to produce strict sulfonation and tar formation which takes place when the acid is highly concentrated, I preferably in accordance with the present invention use an acid which has been diluted with water or other diluting medium so that the strength is lowered, as for example, to 40–60% or 70% as previously noted, although this percentage may be higher or lower depending on the iodin number of the oil, as well as on its other characteristics and the foregoing is merely set forth in an illustrative sense and I do not wish to be limited to any disclosure of precise procedure as laid down herein, but wish to embrace such equivalent methods of treatment or range of treatment as fall within the scope hereof.

After treating the crude product with sulfuric acid of say 50% strength, a stronger acid may follow as the more readily charred bodies may be removed by the more dilute acid and further extraction and refining by stronger acid as 60, 70, or 80% strength may then be brought about. Oxidizing agents such as a somewhat dilute solution of chromic acid may be used to improve the color. Filtration or other suitable contact with charcoal also is useful.

The strength of the sulfuric acid to be employed in producing the product of this invention in its preferred aspects may be conveniently found in a practical manner by treating a series of samples of the spirit obtained from the cracking step with acid of different strengths ranging from about 40% and upward. If a determination of the iodin number is first made to indicate the degree of unsaturation, the effect of sulfuric acid may be ascertained in one of two ways. Either the start may be made with strong concentrated (anhydrous) acid and then progressively diluted acid used until the correct reaction strength is found, or 40% acid may be used at the start and acid of progressively increasing strength employed until the correct reaction strength is found, by this procedure. With cracked material of an iodin number of between 200 and 300 the latter method is best as the more dilute acid is likely to prove the correct reagent for permanent use. With iodin numbers below 100 the former method is recommended. If the strength of the acid is too great for desirable practical operation, especially with the products of high iodin numbers, charring or vigorous carbonization will occur and in such cases the cracked material collecting above the sulfuric acid layer after such treatment is usually discolored to such an extent as to be unsatisfactory in appearance as a commercial article while in the acid layer are frequently found carbonized masses usually discolored to such an extent as to be unsatisfactory in appearance as a commercial article while in the acid layer are frequently found highly carbonized masses.

With the preferred strength of acid as found in this manner, the upper layer of hydrocarbon is normally of a relatively light color and any coloration present is usually fairly well removed by treatment with alkali and washing. When an acid of a strength substantially not permanently discoloring the hydrocarbon has thus been ascertained, such strength of acid may be regularly used in large scale operation under approximately the same conditions, over an indefinite period. Of course slight variations from day to day in the cracked product do not require readjustment of conditions. Once the proper strength of acid is found for the manner of operation in hand no change is usually required over long periods. A slightly larger or smaller proportion of olefins or other unsaturated bodies in the crude cracked spirit does not necessarily call for the modification of the strength of the acid as some latitude in this respect is feasible. A light colored or water-white gasoline is prepared with difficulty from cracked oil running high in readily oxidizable olefins if too concentrated an acid is employed as usually some coloring matter forms which is soluble in the gasolene and which is not readily extracted by alkali and which can be removed by bleaching agents only at considerable expense. Consequently to prepare a clear substantially water-white gasoline free from such discoloring agents, the strength of the acid may be adjusted as indicated in the foregoing so that carbonization will be so slight as not to bring about the objectionable formation of gasolene soluble dyestuffs and the adjustment of the acid to this strength for any given grade of cracked material may be made with small samples first until the desired strength of the acid is found for the particular grade of cracked material under treatment.

Ordinary natural gasolene, as stated, has a low iodin absorption or none at all, while the present product, it will be noted, normally has a relatively high iodin number. In spite of this, the aforesaid treatment renders the product relatively stable. Moreover, generally speaking, it is more volatile than ordinary gasolene. In fact the new product having in one instance, a gravity of say 52° Bé. apparently operates in carburetters equally as well as, or better

than common gasolene of about 54° or 55° Bé. The unsaturated condition of the new product apparently renders it more reactive with oxygen enabling greater ease of ignition and more uniform explosion in internal combustion engines.

At a gravity of say, 54° Bé., for both common gasolene and the preferred product of the present invention, the latter in its preferred form shows greater volatility, diffuses more easily, has a lower flash point and is ignited with greater ease and seemingly is burned more effectively than the former. It appears that a considerable degree of unsaturation is not undesirable if the gasolene has been extracted by acid of predetermined strength as above indicated, as smooth engine operation may be maintained by the use of products of this character. The olefins, etc., which may remain after such extraction, although stable enough to be relatively permanent in storage, are yet apparently sufficiently sensitive to aid in the responsiveness of the fuel when used in internal combustion engines.

My product in its preferred aspects has an iodin number not less than 30, but preferably is higher and even may be in excess of 75 or 100, under some circumstances, and in its preferred form is substantially free from olefins readily forming resinous bodies on exposure to air.

The foregoing description is given in detail but it is to be understood that such illustrative matter is not to be construed as a limitation defining the invention in any narrower sense than is comprehended by the substance of the appended claims.

Thus in the operation of the foregoing process to yield a preferred form of the product involved in the present invention, heavier hydrocarbon material is exposed to a cracking temperature, as for example, by passage of said material through a heated zone to effect decomposition, and the products of such decomposition, particularly the lighter fractions, are subjected to the action of an acid comprising sulfuric acid of predetermined strength; whereby easily oxidizable or attackable olefins are extracted and in adjusting the strength of the acid to suitably extract these or other olefin bodies which are to be removed, employing further extraction with stronger acid if required to remove olefins not extracted by the weaker acid; and my invention thus embraces as the preferred form of the present invention a gasolene substitute or motor spirit consisting of, or comprising cracked gasolene material, that is, gasolene material made by heat decomposition of a heavier oil preferably substantially freed from olefin or kindred bodies of an easily oxidizable or resin-forming character yet containing some unsaturated bodies, and in the preferred form exhibiting an iodin absorption value or number of 30 or over, while preferably or ordinarily having a flash point lower than normal natural gasolene of corresponding specific gravity.

What I claim is:—

1. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies and having greater volatility than gasolene of corresponding specific gravity.

2. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of at least 30 and having greater volatility than gasolene of corresponding specific gravity.

3. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of about 75 and having greater volatility than gasolene of corresponding specific gravity.

4. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies but being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

5. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of at least 30 but being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

6. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of about 75 but being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

7. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies, having greater volatility than gasolene of corresponding specific gravity and being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

8. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series.

9. The herein described motor spirit consisting of gasolene like material of a complex

character containing a substantial amount of unsaturated bodies of the aliphatic series, corresponding to an iodin number of at least 30.

10. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series corresponding to an iodin number of about 75.

11. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series but being substantially free from resinifying olefins.

12. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series corresponding to an iodin number of about 75 but being substantially free from resinifying olefines.

13. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of stable unsaturated bodies.

14. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of stable unsaturated bodies and substantially free from resinifying olefins.

15. The herein described motor spirit of a complex character and substantially water-white color consisting of gasolene like material of a complex character containing a major portion of saturated petroleum hydrocarbons and a substantial amount of relatively stable olefins but being substantially free from olefins readily forming resinous bodies on exposure to air.

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