

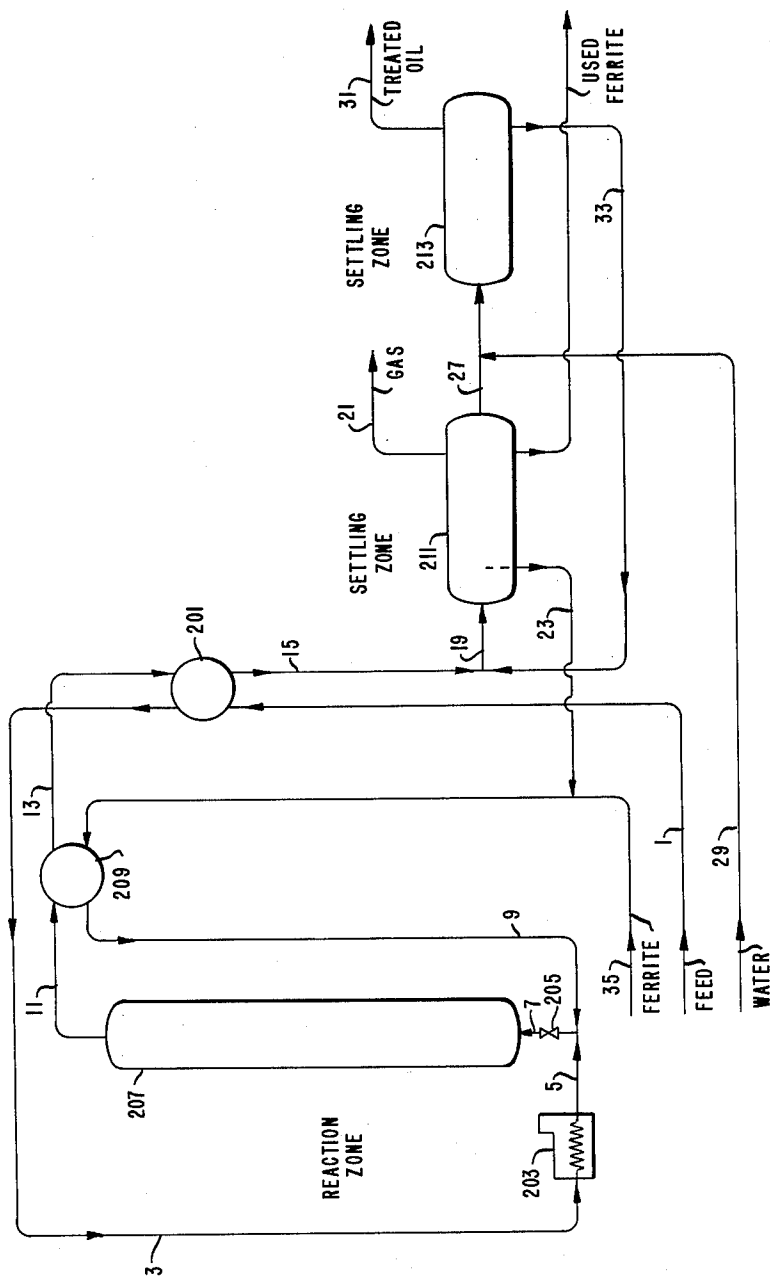
June 9, 1964

J. W. GIBSON ET AL

3,136,714

UPGRADING HEAVY HYDROCARBON OILS

Filed Nov. 10, 1961



INVENTORS:

JOHN W. GIBSON
WILLIAM B. WILSON
GEORGE M. GOOD

BY: *William H. Myers*
THEIR AGENT

1

3,136,714

UPGRADING HEAVY HYDROCARBON OILS

John W. Gibson, Oakland, and William B. Wilson, Pleasant Hill, Calif., and George M. Good, Hillsdale, N.J., assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware

Filed Nov. 10, 1961, Ser. No. 151,497

8 Claims. (Cl. 208—226)

This invention relates to a process for upgrading hydrocarbon oils containing metals and heteroatomic compounds. The invention relates particularly to the processing of heavy hydrocarbon oils containing relatively large amounts of such impurities.

Because of increased demand for petroleum products and because of the reduced supplies of paraffin-base crudes, the petroleum industry today processes largely naphthenic, aromatic, or mixed-base crude petroleum. In addition to being less paraffinic in character, these latter crude oils also contain larger quantities of metals and heteroatomic compounds. It is well known that most of such impurities tend to be concentrated in the heavy oil portions of the crude and particularly in the residual fraction. The long residues which are produced from the usual distillation of crude oil are therefore normally processed further in one of two ways. They are vacuum distilled or extracted in order to separate at least part of the more volatile and normally more valuable portions, or else they are cracked. In either case, the by-product of such processing is a residual fraction having still higher content of metals and heteroatomic compounds.

The disposal of such residuals in the past was facilitated by their extensive use as industrial and marine fuels. However, because of steadily increasing demand for further distillates and also because of restrictions imposed in many industrial areas on the use of such materials because of air pollution problems, there has been a steady impetus to devise methods by which such contaminant-containing heavy oils could be economically upgraded to more valuable products. A solution to the problem of meeting increasing distillates demand is, of course, utilization of one or more of the basic refinery cracking processes, e.g. either thermal or catalytic cracking. Thermal cracking of such high contaminant residuals is of only marginal value since (1) the gasoline produced thereby is usually of inferior quality and (2) the cracked residue, which represents a still sizeable proportion of the yield, is still higher in the same contaminants and is more viscous. Catalytic cracking, on the other hand, is virtually impossible from a practical viewpoint because of excessive contamination of the catalyst by the metallic impurities contained in such heavy oils and because of the excessive formation of coke on the surface of the catalyst.

It is known that heteroatomic materials such as thiophenic compounds, pyrrolic compounds, and pyranlylic materials can be removed by catalytic hydrogenation processes. Such processes, moreover, are also moderately effective in removing metallic contaminants from heavy feeds. Catalytic hydrogenation is currently gaining rapidly in its extent of utilization. It is used widely in the treatment of gasoline, kerosene, light fuel oils (furnace oils), lubricating oils and transformer oils. However, catalytic hydrogenation is basically and inherently a costly process which involves costly catalyst and equipment, and its use is by necessity limited to those stocks which may be hydrogenated economically (1) by virtue of their low contaminants content or (2) by virtue of the fact that they are extremely high value products which can thus bear expensive processing costs.

It is therefore an object of this invention to provide an improved process for the removal of heteroatomic

2

compounds from hydrocarbon oils. It is also an object of the invention to provide an improved process for the removal of metalliferous materials from heavy hydrocarbon oils, particularly residual oils. It is a further object of the invention to provide a process whereby heretofore unsuitable feed stocks are upgraded so that they may be used in conventional catalytic processing operations. It is a particular object of the invention to provide a process for treating residual hydrocarbon oils whereby greater quantities of such oils may be catalytically cracked economically and practically. These and other objects will be apparent from the description of the invention.

The figure is a schematic flow diagram illustrating a preferred method for practicing the process of this invention.

Now, in accordance with the present invention, a process for the upgrading of heavy hydrocarbons and residues comprises contacting the oil in liquid phase at temperatures between about 375 and 475° C. for 1–90 minutes with at least one alkali metal ferrite and separating from the contacted mixture an oil phase having a substantially reduced content of contaminants. Still in accordance with this invention, a preferred version of the process comprises regenerating the at least partially spent ferrite and recycling it for contacting with further quantities of the heavy hydrocarbon oil to be upgraded. One important aspect of the invention comprises the drastic viscosity reduction of the treated product. Another aspect of major interest is the conversion of a fraction of the oil to phenolic compounds capable of reaction with epoxides to form resinous reaction products.

One of the unexpected features of the invention comprises the substantial reduction in iron content of the oil, in spite of the fact that the treating agent, i.e. the ferrite, contains iron.

The feed to the present process may be any higher boiling hydrocarbon oil at least about 50% by volume of which boils above about 450° F. Though even lighter hydrocarbons can in principle be processed, the present process is most advantageous for treatment of oils containing materials which cannot be distilled in commercial equipment without extensive cracking, e.g., residual materials and hydrocarbon oils containing asphaltenes, resins and the like. The process finds its greatest utility in the treatment of stocks containing appreciable amounts of hetero atoms and/or metals. It is, therefore, particularly useful for the treatment of reduced crudes, vacuum residues, cracked gas oil residues and the like which cannot otherwise be deeply flashed without excessive carryover of metal contaminants. In addition, certain crude petroleum oils which contain only small amounts of gasoline and kerosene boiling range hydrocarbons and which have been topped to remove lighter components may also be processed. Certain petroleum crude oils, oils from tar sands and oils from shale thus may be processed without being extensively reduced.

The alkali metal ferrites which are to be used as the principle treating agent in the process of this invention comprise particularly the ferrites formed between one mol of alkali metal oxide and one to nine mols of an iron oxide, preferably Fe_2O_3 . The preferred alkali metal ferrites are those having one to two mols of ferric oxide per mol of alkali metal oxide and the preferred species comprises equimolar ferrites of potassium oxide and ferric oxide. Ferrites are not mere physical mixtures of the alkali metal oxide and iron oxide but, on the contrary, are calcined products of the two oxides usually prepared by calcining alkali metal compounds such as a carbonate with the iron oxide at temperatures in the order 750–1000° C. Mixtures of alkali metal oxides may be present

in the ferrite, such as mixtures of 1-10 mols of 1 alkali metal oxide per mol of a second alkali metal oxide, this mixture in turn being calcined with iron oxide to form a ferrite.

The proportion of alkali metal ferrite to be employed in the process of the invention will depend, in part, on the activity of the specific ferrite employed and upon the exact nature of the oil being treated. Normally the ferrite will be present in a weight ratio of ferrite to oil between about 0.1 and 2.5, preferably 0.5 to 2.0.

The temperature at which the operation is carried out is important. Qualitatively, the preferred temperature is that of incipient cracking, i.e., where thermal cracking would normally begin to take place, but below that temperature at which extensive thermal decomposition occurs. However, especially when gaseous products are removed, more drastic cracking can be accepted. The temperature of incipient cracking varies with the nature of the particular oil being processed. In all cases for satisfactory operation of the process of the invention, the final temperature will be within about 375 to about 475° C. For most heavy oils and residues the preferred temperature of reaction is from about 390° C. to about 460° C.

Because the reactions which take place are largely in the liquid phase, the pressure is generally not an important factor in the process of the invention. However, it is desirable usually to suppress vaporization of the reactants in order to minimize reactor size. Consequently, superatmospheric pressures are preferred. Any higher pressures can be used if desired, but it is preferred to employ operating pressures of at least 200 p.s.i.g. but below about 1,500 p.s.i.g. Above this pressure the economic advantage of lower reactor volume is offset by the higher cost of such high pressure equipment.

Contacting of the oil and the normally solid pulverulent ferrite may be carried batch-wise, as in an autoclave, or continuously. Continuous operation is preferred for commercial application of the process. Intimate contacting of the oil feed and ferrite is important in order to obtain the unique advantages which characterize the process. It is therefore preferred to impart a high degree of turbulence to the materials as they are mixed at least in the initial stages of the contacting. When in-line mixing of the ferrite and feed is employed, it is preferred to use a mixing valve downstream of the injection point of the two components. The ferrite may be injected as a dry powder or more preferably, in the form of an oil suspension. If a conventional pressure reaction vessel is employed, both the initial mixing and sustained turbulence of the system may be obtained by the use of one or more turbine mixers.

The required contact time of the oil with ferrite varies widely depending upon the particular stock being processed and the desired degree of improvement in the stock for liquid process is being employed. The contact time will also vary with the activity of the ferrite and with the temperature being utilized during contacting. Generally, however, the contact time will be between 1 and 90 minutes, 2-15 minutes being the range of contact time most generally useful. The contact time will vary, not only with the oil and ferrite being used, but also with temperature. Thus, in many cases, contact time of 1 hour at 375° C. would have roughly the same effect as 1 minute at 475° C.

During the mixing and reaction of the ferrite with the feed, the ferrite, being essentially insoluble in the oil, remains as a separate phase, and contacting is facilitated at times by depositing the ferrite on an essentially inert material, such as, alumina or silica or combinations of these, as well as upon inert materials, such as clays and the like. Extraneous normally catalytic materials (which may or may not perform a catalytic function in the present process) may be present together with the ferrite in physical admixture therewith or even as a component part of the ferrite, such as chromium oxide, zirconium

oxide, etc. Nickel or cobalt oxides may be used in place of or in addition to iron oxides.

It will, of course, be recognized that the ferrite may contain sizeable amounts of materials other than the calcined combination of alkali metal oxide and iron oxide dependent in part upon the previous use of the ferrite such as in a prior contacting treatment with a residual or heavy oil. In such a case the ferrite may be contaminated or mixed with carbonate, sulfides, particles of coke, metals and soluble carbonaceous compounds such as alkyl phenol. These are preferably removed by a regenerating treatment, at least in part, following each contacting period of the ferrite with hydrocarbon oil but for commercial purposes it is not essential that the ferrite be completely regenerated after each pass. If the ferrite and oil are contacted countercurrently, the oil near the inlet may contain a greater concentration of the alkali metal ferrite with lesser amounts of carbonate and sulfides while the reverse ratio of materials may be present near the outlet of the system. When part of the ferrite is recirculated, either with or without regeneration, it is preferably fortified by the addition of either or both additional alkali metal ferrite or additional alkali metal oxide if a calcining procedure is adopted for regeneration of the catalyst.

REMOVAL OF HETEROATOMS

Probably the most important aspect of the use of the process for the removal of heteroatoms from heavy oils and residues, is the removal of sulfur. It is appreciated that it has many times been suggested to remove sulfur compounds from various oils by treating them with aqueous caustic or solid caustic and that caustic treatment of oils is frequently applied in the refining of oils, particularly light oils, and materials previously treated with acid. The purpose of such treatment has been either to neutralize acidic materials formed or left from the acid treatment or to remove phenols, naphthenic acids, or other acidic substances in the oil. Most oils, and particularly the lighter oils, contain small amounts of highly odoriferous mercaptans, which are acidic in nature, and which are removed fairly extensively with aqueous alkali.

Such treatments are, however, wholly unrelated to the present process. The heavy oils and residues with which the invention is concerned do not contain any appreciable amount of mercaptans or other acidic sulfur compounds and such treatments as were common heretofore are ineffective in bringing about any material reduction in their sulfur content. Thus, the sulfur compounds present in the oils treated by the process of the invention are refractory compounds, e.g., benzothiophenes, having no appreciable acidity. Accordingly, the sulfur therein is not removed as, for example, alkali metal mercaptide but as an alkali metal sulfide, which necessitates scission or cracking of the sulfur-containing molecules in the oil. Thus, chemically the desulfurization problem of heavy oils and residuals is the rapid removal of benzothiophenic and dibenzothiophenic sulfur, which comprise from 60 to 85% of the sulfur compound present in most residues. In fact, the major reason that hydrodesulfurization of residues is usually impractical is that the known hydrogenation catalysts have such low catalytic activity for removing these types of sulfur from the more complex higher molecular weight compounds present in residues, e.g., asphaltenes, and that very low space rates are needed. Under such conditions, the deactivation of the catalyst by coke is excessive.

Referring to the drawing, a straight run reduced residue is passed by means of line 1 to heat exchanger 201 wherein the residue is heated by exchanging heat with reactor effluent, which is described hereinafter. The heated residue material is passed by means of line 3 to furnace 203 where it is heated still further. The exit feed from the furnace is mixed with ferrite (which is introduced by

5

means of line 9 as an oil slurry). The mixture of feed and ferrite are passed through line 7, which contains a mixing valve 205 to effect intimate mixing of the residue with the ferrite to reaction zone 207. The reaction zone 207 consists of one or more parallel reaction chambers

appropriately lined to avoid corrosion from the reaction mixture and so sized that the reaction mixture may have a residence time within the range specified hereinbefore. The ferrite may be injected as a powder or as an oil slurry, preferably having been passed by means of line 35 through heat exchanger 209 wherein it exchanges heat with the hot reactor effluent. Thereafter it passes by means of line 9 to line 7 where it is mixed with residue feed as described before.

The reaction mixture subsequent to the residence period within reactor 207 is passed by means of line 11 to heat exchanger 209 wherein it exchanges heat with ferrite from line 35 and is cooled from the reaction temperature thereby. The partially cooled reaction mixture is passed further through line 11 to heat exchanger 201 wherein it exchanges heat with incoming feed and is cooled still further. The cooled mixture of at least partially spent ferrite and treated heavy oil is passed by means of line 19 to a settling zone 211. Settling may be expedited by dilution of the reaction mixture with either a lower boiling hydrocarbon or with water. In the settling zone 211 the mixture of reacted ferrite, treated residue and any diluent settles into at least two layers. The upper layer in the settling zone 211 comprises a layer of treated oil with small amounts of possibly entrained ferrites and impurities. The lower layer consists of a layer of ferrite suspended possibly in water if the latter had been injected (through line 33) as a settling medium. An interfacial "rag" comprising a concentrate of at least partially spent ferrite and oil may be withdrawn through line 23, mixed

6

metal oxide in such an amount that the regenerated ferrite contains alkali metal oxide in calcined combination with iron oxide in a ratio of 1 mol of alkali metal oxide to 1-9 mols of iron oxide. This product may, in turn, be recycled for use in reaction zone 207, preferably by means of line 35.

The upper layer contained in settling zone 211 is withdrawn through line 27 and mixed with a diluent which may be either an immiscible liquid such as water or a low boiling hydrocarbon such as heptane, the mixture of oil and diluent being passed to a second settling zone 213 wherein the mixture is settled into two distinct phases with little or no interfacial emulsion between. The lower layer, containing any residual traces of ferrite, is withdrawn through line 33 for regeneration or recycling. The treated oil product which comprises the upper layer in zone 213 is passed by means of line 31 to further processing such as catalytic cracking, vacuum distillation, catalytic hydrogenation and the like.

The following examples illustrate preferred aspects of the present invention. The ferrites utilized in the examples were prepared by combining an alkali metal carbonate and iron oxide and calcining at 800° C. A feed consisting of 89% Los Angeles Basin Ventura and 11% Four Corners crudes and which contained 1.91% sulfur was treated with a number of different ferrites under the conditions listed in Table I below. For comparison, one run was made with a physical mixture of sodium carbonate and Fe₂O₃. This showed that the removal of sulfur was only 19% as compared with 29-63% sulfur removal when ferrites were employed. It is noteworthy that under some conditions, especially when employing potassium ferrite, vanadium removal was substantially complete, while substantial amounts of the nitrogen and iron were also removed by the treatment.

Table I

USE OF SODIUM AND POTASSIUM FERRITES TO DESULFURIZE RESIDUES

Reagent	Temp., °C.	Time, min.	Re-agent to Oil Ratio	Final Pressure, p.s.i. ^a	Percent Feed		Recoveries		Percent Removal of				Product		Analyses
					Coke ^b	Gas	Oil ^c	Total Products	S	N	V	Fe	Percent Alkali Metal	Precipitation Index	
Na ₂ O-Fe ₂ O ₃ -----	425	15	0.5	335	3.3	1.7	88.1	93.1	29	7	46	40	0.09	57	Filtered Product.
Na ₂ CO ₃ +Fe ₂ O ₃ ^d -----	426	15	0.5	405	5.2	1.8	90.5	97.5	19	12	5	45	0.0005	50	Do.
K ₂ O-Fe ₂ O ₃ -----	427	15	0.5	385	7.9	1	89.8	98.7	37	27	95	45	0.08	50	Do.
K ₂ O-Fe ₂ O ₃ -----	427	15	1.0	475	7.1	1	91.3	99.4	36	23	94	32	0.10	33	Do.
K ₂ O-Fe ₂ O ₃ -----	452	15	1.0	1,050	-----	-----	67.7	89.1	63	57	99	90	0.12	-----	Total Product.
K ₂ O-Fe ₂ O ₃ -----	426	45	2.0	400	-----	-----	84.0	100.0	48	43	88	0	0.03	-----	Do.

^a No initial hydrogen.

^b Coke+carbonate.

^c About half the oil was immediately recoverable by filtration, the remainder being extracted by toluene washing.

^d Not converted to ferrite.

with fresh ferrite in line 35 and recycled to the reaction zone 207. Gaseous products are formed during the reaction step and are collected in the upper part of the settling zone 211 from which they are passed by means of line 21 to further treating, recovery or disposal.

The lower layer of at least partially spent and contaminated ferrite is drawn off through line 25 for regeneration, in which case it may be recycled through the process with fresh ferrite in line 35 or for disposal. Regeneration may comprise calcining the mixture of at least partially spent contaminated ferrite at temperatures of 750-1000° C. whereby substantially all the sulfide and carbonates are removed and carbonaceous deposits are burned off. Water may be injected as such or in the form of steam prior to or during regeneration at calcining temperatures. The calcined product may still contain appreciable amounts of sulfides or these may be completely reconverted to oxide and calcined with iron oxides to form ferrites. Alternatively, the regenerated product may be modified by the presence of or addition to an alkali

Table II

DESULFURIZATION OF RESIDUES WITH FERRITES

Pressure: Initial 500 p.s.i.g. H₂

Reactor: 250 cc. stirred autoclave

	Time, min.	Temp., °C. ^a	Re-agent-to-Oil Ratio	Sulfur in Product, Percent w.	Vanadium, p.p.m.	Desulfurization, Percent of Feed Sulfur	Recovery of Oil, Percent w.
60 Ferrite b-----	37	420	1:2	0.77	31	54	94
Thermal-----	60	415	-----	1.15	27	33	92
65 Fe ₂ O ₃ -----	60	412	1:2	1.10	-----	36	91

^a Temperatures varied from 410-425° C. during the operating period.

^b 7% K₂O, 39% Na₂O, 1.5% Cr₂O₃ and 52.5% Fe₂O₃.

The contacting was carried in a pressure vessel with stirring and the spent ferrite removed from the treated oil by filtration and dilution of the oil with a lower boiling solvent to recover still further quantities of oil.

EXAMPLE

A special catalyst was prepared by calcining sodium

7

carbonate with a catalyst containing potassium oxide, chromium oxide and ferric oxide, the calcination being conducted at 900° C. The same straight run residue as utilized in the previous example was contacted with the catalyst so prepared, two parts of the residue being employed for one part of the ferrite. The data obtained are given in Table II in comparison with other treatments known to cause desulfurization.

An advantage in using ferrites due to the easy removal of CO₂ by calcination is shown in the following tabulation.

Table III

Material	Sulfur, Percent w.	Carbonate, Percent w.	Na, Percent w.	Total Carbon, Percent w.
Spent Na ₂ O, Fe ₂ O ₃	1.44	1.5	17	10.7
Above calcined at 850° C., 16 hours.....	1.27	0.2	20	0.2

The data show that carbonate and carbonaceous material are effectively regenerated or removed and that about 25% of the sulfur is taken off. The use of steam and/or more severe calcining conditions remove further quantities of sulfur.

We claim as our invention:

1. A process for upgrading heavy hydrocarbon oils at least about 50% by volume which boils above 450° F. containing contaminants of the group consisting of metals and heteroatomic compounds of sulfur and nitrogen which consists of contacting the oil in liquid phase at temperatures between about 375 and 475° C. for 1-90 minutes with at least one alkali metal ferrite and separating from the contacted mixture an oil phase having a substantially reduced content of contaminants.

2. The process according to claim 1 wherein the weight ratio of ferrite to oil is between about 0.1 and 2.5.

3. The process according to claim 2 wherein a pressure in excess of 200 p.s.i.g. is utilized during contacting.

8

4. The process according to claim 1 wherein the ferrite is a potassium ferrite.

5. The process according to claim 1 wherein the ferrite is a sodium ferrite.

6. The process according to claim 1 wherein the ferrite is a sodium potassium ferrite.

7. A process for upgrading heavy hydrocarbon oil at least about 50% by volume which boils above 450° F. containing contaminants of the group consisting of metals and heterocyclic compounds of sulfur and nitrogen which consists of the steps:

(1) intimately contacting the oil in the liquid phase with an alkali metal ferrite, the weight ratio of ferrite to oil being from 0.5 to 2.0 at a temperature between about 390-460° C. and a pressure of 200-1500 p.s.i.g. for 2-15 minutes, thus forming a reaction mixture of at least partially spent ferrite and reacted oil product;

(2) separating the reacted oil product from the at least partially spent ferrite in a separation zone;

(3) calcining the separated ferrite at a temperature between about 750-1000° C. whereby the alkali metal ferrite is at least in part regenerated;

(4) and recycling the regenerated ferrite for further use in step (1).

8. A process according to claim 7 wherein an alkali metal compound is mixed with the at least partially spent ferrite and the mixture so formed is calcined, the compound being one which forms an alkali metal oxide at the calcining temperature and being added in such an amount that the calcined product containing 1-9 mols Fe₂O₃ per mol of alkali metal oxide.

References Cited in the file of this patent

UNITED STATES PATENTS

1,959,467	Fields	May 22, 1934
2,090,190	Dolbear	Aug. 17, 1937
2,559,323	Spillane	July 3, 1951