(No Model.) 2 Sheets—Sheet 1.

H. FRASCH.

REFINING CANADIAN OR SIMILAR PETROLEUM.

No. 543,619. Patented July 30, 1895.

FIG. 1.

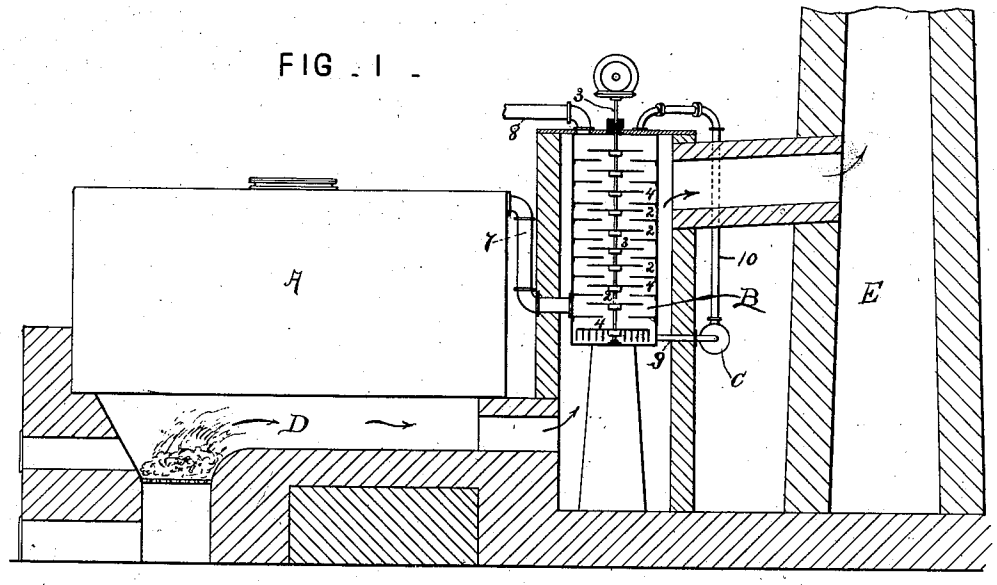
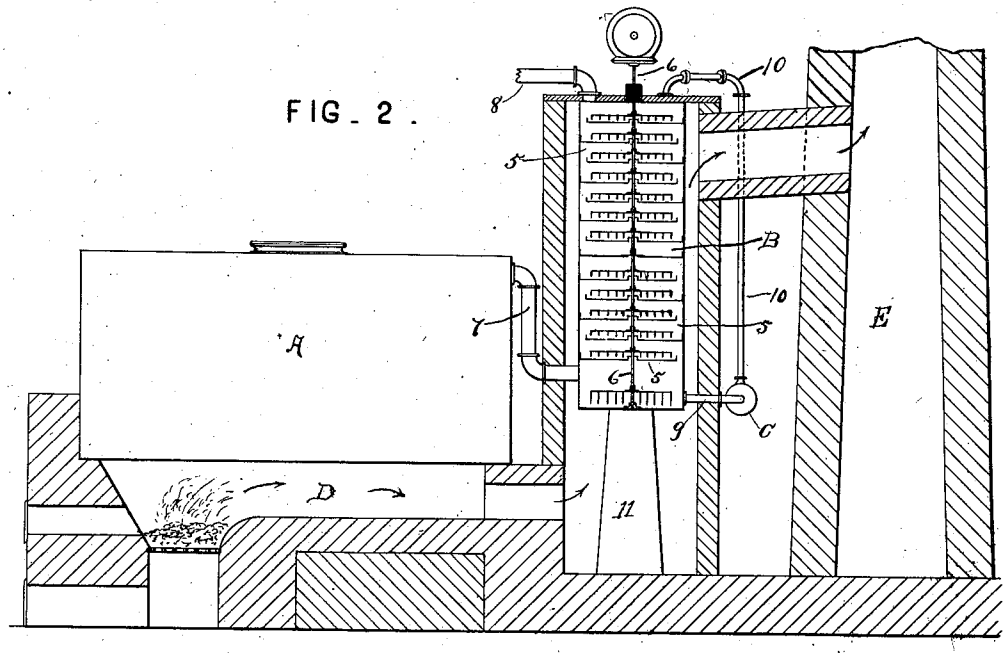


FIG. 2.



Witnesses
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(No Model.) 2 Sheets—Sheet 2.

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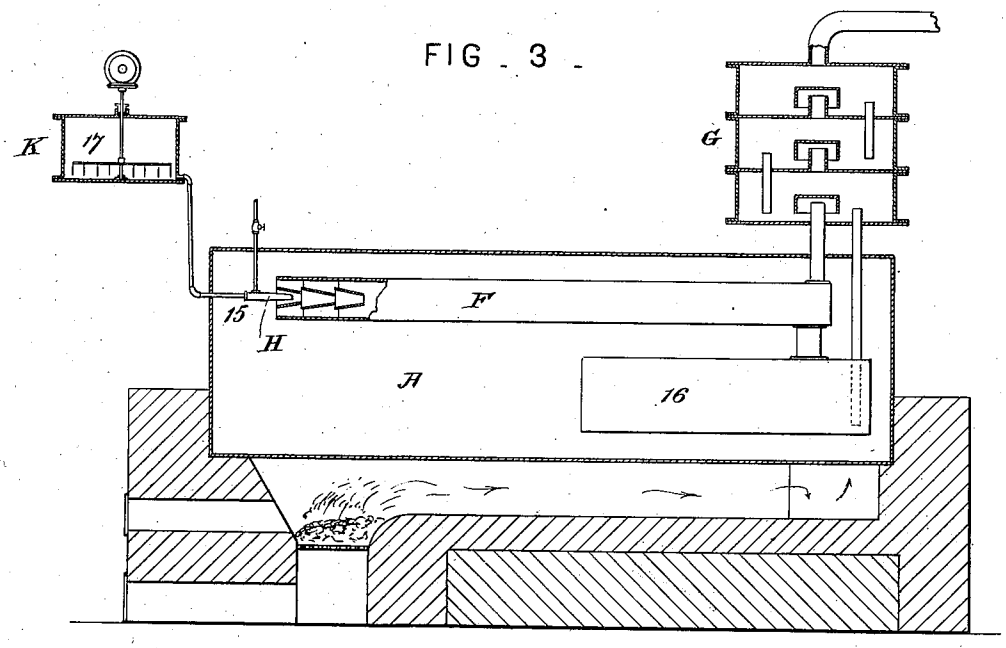
FIG. 3.



Attest:
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UNITED STATES PATENT OFFICE.

HERMAN FRASCH, OF CLEVELAND, OHIO, ASSIGNOR TO THE SOLAR REFINING COMPANY, OF OHIO.

REFINING CANADIAN OR SIMILAR PETROLEUM.

SPECIFICATION forming part of Letters Patent No. 543,619, dated July 30, 1895.

Original application filed February 15, 1888, Serial No. 264,131. Divided and this application filed January 23, 1891. Serial No. 378,818. (No specimens.)

To all whom it may concern:

Be it known that I, HERMAN FRASCH, a citizen of the United States, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented certain new and useful Improvements in Refining Canadian or Similar Petroleum, of which the following specification is a full, clear, and exact description.

This invention relates to the treatment of Canadian and similar petroleum—such, for example, as that found at Lima, Ohio. This oil requires a different treatment from the ordinary American oil, because of the sulphur compounds which it contains and which give it its penetrating disagreeable odor and render it unfit for burning in lamps unless deprived of said compounds. The sulphur is present in these oils in considerable proportions—say upward of one-half of one per centum ($\frac{1}{2}$ of 1 %)—mostly in chemical combination, and some at least of the sulphur compounds are essentially different from those which occur in other oils and are retained with great tenacity. These peculiar sulphur compounds have received among the workers in the oil of this class the suggestive name of "skunk." To deprive these oils of their peculiar sulphur compounds or skunk is the object of the present invention.

The large proportion of sulphur will generally distinguish Canadian and similar skunk-bearing petroleum from other oils, but a further distinction may be found in the nature of the sulphur-containing bodies therein. They give to the oils the property of dissolving lead-oxide, (litharge.) So far as I am aware no mineral oil, whether undistilled or distillate, other than Canadian or similar skunk-bearing petroleum possesses this property of dissolving litharge. Ordinarily petroleum can be made to dissolve litharge by the addition to said oil of a fat acid, such as oleic acid or rosin, but the Canadian or skunk-bearing pretroleum will dissolve lead oxide (litharge) without such addition. Further, the skunk-bearing oil has a peculiarly bad odor, which disappears on saturating the oil with lead-oxide. On precipitating the lead from such solution by means of sulphur, the bad odor does not reappear, neither does the oil regain the property of dissolving lead-oxide. On distillation, however, of the oil from which the lead has been precipitated, as just described, the malodor reappears and the oil will again dissolve lead-oxide, showing that the skunk remained even after the malodor disappeared. The malodor also reappears on burning and the lamp-chimneys become smoked. Moreover, while the sulphur existing in the oil as skunk is not removed by treating the oil with sulphuric acid and alkali, (which treatment will remove practically all the sulphur existing in Pennsylvania oil,) it is also true that after the removal of the skunk from Canadian and similar petroleum by the present invention there yet remains in said petroleum (now become sweet and incapable of dissolving lead-oxide even after redistillation) sulphur in such form or forms that a repeated application of the skunk-removing process fails to eliminate it or materially to reduce its proportion, while it can be separated almost entirely by treatment with sulphuric acid. Skunk-bearing oil therefore is radically different from other mineral oils in respect to the sulphur bodies therein, said bodies giving to the skunk-bearing oil peculiar properties, as hereinbefore mentioned, and being not removable by the refining means in common use which do remove the sulphur from American petroleum, while at the same time means efficient to remove skunk do not take out sulphur bodies removable by said refining means in common use on American oil, so that the utility of certain reagents or modes of treatment in desulphurizing other mineral oils is no proof of an ability to remove the skunk of Canadian and similar petroleum, nor does an ability to remove skunk constitute proof of a given process being capable of replacing the ordinary means of desulphurizing oil.

Heretofore it has been customary in Canadian refineries (and the same treatment has been employed in parts of the United States) to take the burning-oil distillate, which has been subjected to the action of sulphuric acid and washed with water, and to treat the same with a solution of plumbate of soda in order to deodorize it, and then to add sulphur in

powder in order to restore the color which the plumbate solution has turned to a yellow or brown and cause the precipitation of the lead, leaving the oil above it white and clear. The solution of soda settles to the bottom. The objections to this old deodorizing process are twofold: First, an excess of sulphur is liable to be added in the second stage, which is injurious to the oil, and, secondly, the treatment is not thorough, for it does not remove the sulphur compounds or skunk, but only renders the same inodorous and incapable of further uniting with the lead oxide of the plumbate solution. On distillation the sulphur compounds in the oil again became malodorous and the oil is discolored by the addition of the plumbate of soda solution.

In a prior application filed February 21, 1887, and serially numbered 228,403, (on which Patent No. 378,246 was granted me February 21, 1888,) I have described a process not open to these objections for refining oil of the Canadian or Lima class by distilling the same with suitable oxides or compounds mixed with or dissolved in the oil under treatment. The present invention is, as it were, a supplement to or complement of that process. I have discovered that the refractory sulphur compounds or skunk of Canadian and similar oils are decomposed by suitable metallic oxides or compounds without necessarily having such an oxide or compound dissolved in or mixed with the oil in distillation by subjecting the vapors after leaving the liquid oil to the action of the said oxides or their compounds in an undissolved condition.

The carrying on of the process of purification by acting upon the vapors after they have left the oil in or from which the said vapors have been generated possesses advantages over the process described in my said patent. One advantage consists in the ability to remove skunk from the vapors of crude oil without experiencing any difficulty from the presence of solid matter in the tar. The tar being mixed with the residue to be revivified leaves an unnecessary mass of combustible matter in such residue. The presence of solid material in the oil in the still moreover gives rise, irrespective of the question of the tar, to difficulties which are not necessarily attendant on an outside vapor treatment, since this does not require the presence of solid matter in the oil. The vapors may be brought into contact with the undissolved oxides or compounds in any ordinary or suitable way. The undissolved oxide or compound may be injected into the vapors or be showered through the vapors, or vapors may be passed through the oxide or compound supported on shelves or other suitable supports in a dry state or more or less saturated with a liquid. The oxides of lead, bismuth, cadmium, mercury, copper, and silver are well suited to the purpose. Ferric, stannic, and antimonic oxides, cuprous oxide, and the oxides of nickel, cobalt, manganese, and zinc are of little value by themselves, but may be used in connection with those first mentioned. Suitable compounds are the readily decomposable oxygen compounds or oxygen salts in general of the metals which are precipitable by hydrogen sulphide in acid solution, such as the carbonates, manganates, chromates, borates, sulphates, and the like of such metals.

The vapors to be treated in accordance with the present invention can be generated from the crude oil or from any desired distillate. The purification or refining is, however, specially intended for burning oil having a boiling-point of 212° Fahrenheit or over.

The liquid condensed from the vapors which have thoroughly been brought into contact with the oxide or compound, so as to give it opportunity to act upon all the sulphur compounds or skunk will stand the plumbate of soda test. I find, however, that the condensed liquid or distillate purified from skunk, although it will stand the plumbate of soda test, yet contains sulphur compounds which I believe to be peculiar to oil treated in this way and which impair the value of the oil by causing a chimney-deposit when burned in a lamp. These products, like the similar or identical ones from distilling the oil with the purifying oxide or compound mixed with or dissolved in the same, are essentially different from skunk and are, as I have discovered, removable by treatment with sulphuric acid, washing with water, and neutralizing as customary in refining American petroleum.

The metallic sulphur compounds which are formed by the reaction with the sulphur-containing impurities of the vapors, as above set forth, can be revivified by roasting and oxidation, and these revivified residues can be employed successfully to treat new vapors of Canadian or Lima or similar skunk-bearing oil.

In my original application, Serial No. 264,131, filed February 15, 1888, of which the present application is a division, description was given of the removal of skunk from petroleum by subjecting the skunk-bearing vapors after they had been given off to the action of an oily or resinous liquid holding the oxides or compounds in solution or solution and suspension, as well as by subjecting such vapors to the action of the undissolved oxides or compounds. After the filing of the present divisional application the said original application was so amended that Letters Patent No. 487,119 were granted thereon November 29, 1892, for the process of using the oily or resinous liquid holding the metallic oxides or compounds in solution or solution and suspension therein. The apparatus shown in the accompanying drawings is more particularly intended for use with such oily and resinous liquid holding the metallic oxides or compounds in solution or solution and suspension, but (modified as explained below) it may be used with the unsolved oxides or compounds.

Fig. I is a sectional view of an oil still and purifier. Fig. II is a similar view of a slightly modified form of the same apparatus, and Fig. III is a similar view of another form of apparatus.

Referring to Figs. I and II, an ordinary still A is provided with a column B which has baffle plates or trays and stirrers, as common or at least known in various chemical arts. In Fig. I the baffle-plates 2 are in the form of circular disks, which are mounted horizontally on an upright central shaft 3, and the baffle-plates 4 are in the form of rings fastened to the walls of the column B and projecting inward between the disk plates 2. In Fig. II the trays 5 are fastened to the walls of the column, and the openings for the passage of the vapors are formed at the opposite sides of alternate trays, and the shaft 6 is provided with stirrers which dip into the trays. In all the figures the top of the still A is connected by a vapor-pipe 7 with the column B, and at the top of the latter there is a pipe 8 for conveying the purified vapors to the condenser. (Not shown.) A pipe 9 leads from the base of the column B to the pump C, and a pipe 10 from the said pump C to the top of said column. The shafts 3 and 6 are rotated by bevel-gear, and the column B, which rests on a pillar 11, is heated by the products of combustion from the fire-chamber D under the still on their way to the chimney E. The column B should be of such size as to bring the vapors sufficiently into contact with the purifying material. If the still be such as commonly used to distill a charge of one hundred barrels of oil, the column B may be, say, ten feet high and four feet in diameter with the baffle-plates or trays about six inches apart.

In operation the still may be charged with, say, one hundred barrels of oil composed of, say, fifteen per centum of heavy oil of from 36° to 39° Baumé and the remainder burning-oil distillate boiling at 212° Fahrenheit or over. For working with the oily or resinous solution, as in my said Patent No. 487,119, the column may be supplied with, say, five barrels of heavy impure or skunk-bearing Canadian or similar oil, mixed with, say, one barrel of rosin, five hundred pounds of plumbic oxide, (litharge,) one thousand pounds of cupric oxide, (black oxide,) and one thousand pounds of plaster-of-paris, the oxides and plaster being finely ground and bolted. The rosin and part of the oxides dissolve in the oil and the rest of the oxides and plaster are kept in suspension therein. The oil with the matter in solution and suspension therein flows over the baffle plates or trays, which trays become filled and collect in the bottom of the column B. After or before the oil is introduced the pump is started, which draws off through the pipe 9 the oil holding the oxide in solution and suspension therein and returns it to the top of the column B through the pipe 10. The shaft 3 in the column is also rotated. The rotation of the disks 2, Fig. I, throws the liquid and solids off onto the rings 4, from which they descend to the next disk by gravity, the flow of the liquids being sufficient to sweep away the solid particles; but, if desired, mechanical devices or scrapers could be employed to sweep or scrape the surfaces of the baffle-plates, as well known in chemical apparatus, wherein gases or vapors are to be brought into contact with liquids holding solid particles in suspension therein. The rotation of the shaft 3 also keeps the material stirred up in the bottom of the column B by means of an ordinary blade or paddle The rotation of the shaft 6, Fig. II, keeps the material stirred up in the trays 5 and at the bottom of the column. The still A and the column B being charged and the pump C and shaft 3 or 6 in column B being started, the still A and column B are heated, the former to evaporate the burning oil therein and the latter to prevent or diminish the condensation of the vapors from the still. The vapors pass through the pipe 7 into the lower part of column B, through which they then pass upward, and are in their passage brought into intimate contact with the liquid holding the oxides in solution and suspension, said liquid with the oxides flowing in the opposite direction over the baffle plates or trays and falling from one to the other through the rising vapors. The vapors escape by the pipe 8 to the condenser. The passage of the vapors through or over the liquid enables the oxides to act on the skunk in said vapors with the formation of metallic compounds which remain in the liquid and certain new bodies which pass of with the vapors. A constant stream of the oil having the oxides dissolved and suspended therein is introduced at the top of the column B and drawn off at the base. The liquid drawn off is returned to the column, the whole or a portion of the precipitated or solid matter in suspension being removed and replaced by fresh oxides at each round or from time to time. As the metal of the oxides in solution combines with the sulphur of the skunk and become insoluble fresh oxide enters the solution, the same being supplied from the matter in suspension. The still is or may be supplied continuously or from time to time.

It is not necessary to have the column B heated otherwise than by its proximity to the still A and the passage through it of the vapors from said still; but in that case the condensed vapors must be taken care of, either by returning them to the still or otherwise. If solid matter is allowed in the still, either by entering in that state from the column B or by precipitation in the still, the latter should be provided with an agitator to keep it from settling.

The plumbic or the cupric oxide could be used alone—say thirty-three hundred pounds of plumbic oxide or twelve hundred pounds of cupric oxide—or one or both could be replaced by or used in connection with another

or others of the specified agents. The plaster and the resin may be omitted.

For working with undissolved oxides or compounds no liquid need be used, but the powdered oxide or compound may be fed through the purifier-column B, being withdrawn at the bottom and returned at the top by well-known conveyers.

According to another plan of working (see Fig. III) the still A is provided inside with a large pipe F, which communicates with the interior of the still through the opening 15, and also with a small column G, such as used in rectifying alcohol on top of the still, and with a small vessel or receiver 16 inside the still. A steam-injector or steam-jet aspirator and compressor H sucks the vapors from the upper part of the still A and forces them through the pipe F into the bottom of the column G. The injector H also forces into the pipe F and among the vapors therein the purifying oxide or compound finely divided and in the form of a powder. The arrangement shown for supplying the injector with purifying material is intended for use with an oily or resinous solution holding the oxide or compound in suspension, and consists of a reservoir K provided with a stirrer 17 and connected with the injector H by a small supply-pipe. More or less of the oxide is forced with the vapors into the column. What does not so pass is carried into the small vessel or receiver 16, the object of which is to keep the sediment from the bottom of the still. This material could be allowed to run into the still, but in that case the latter should have an agitator; or it could be discharged outside of the still, to be returned or otherwise disposed of. The column G has an overflow at the bottom, which discharges into the receiver 16. The oil or condensed vapor in this receiver is volatilized again and passes in vapor form into the pipe F, and then into the column G. The large pipe F may have an opening into the vapor-space at each end, so as to circulate the vapors through the pipe, as well as force them into the column G. The steam-jet to force the vapors could be used in the arrangements described with reference to Figs. I and II. Other modes of bringing the vapors into contact with the purifying agents have been indicated in the first part of this specification.

The larger the proportion of skunk in the oil the more thoroughly should the vapors be brought into contact with the purifying agents; and if the process is carried on by batches—that is, without a constant renewal of the oxide or compound—care should be taken to have the amount of purifying agent larger than necessary to decompose all the skunk. The weight of oxides given when used in solution or solution and suspension in an oily or resinous liquid would be ample for one hundred barrels of oil containing about one-half of one per centum of sulphur.

The vapors from the purifying apparatus are received in a condenser (not shown) and the condensed liquid is washed with sulphuric acid, or it may be used without such washing.

The solid sulphur-containing residue from the above operation or from an analogous operation is roasted and oxidated, and after grinding and bolting is used like fresh oxide.

In order to revivify the purifying agent or agents the solid residue is thrown into the front part of a roasting-furnace a portion at a time and ignited. The combustion of the sulphur-containing residue furnishes all the heat necessary for roasting. The air will supply the oxygen, so as to effect the revivification at one operation. As each fresh portion is added the portions previously introduced are pushed back until the whole charge has been transferred to the furnace. The mass becomes red hot and is thoroughly roasted and oxidated. The fine division of the powder and its composition insures a perfect and quick roasting. It is stirred until below red heat, and is then discharged to be reground for use again.

I do not claim herein the apparatus described. It forms the subject of my application, Serial No. 289,746, filed November 1, 1888, on which Letters Patent No. 490,144 were granted January 17, 1893; nor do I claim herein the revivification of the residue of the revivified residues, as such matter forms the subject of my application, Serial No. 284,830, filed September 7, 1888, on which Letters Patent No. 500,252 were granted June 27, 1893; but the use of the revivified residues, as herein described, is included in the present invention; nor do I claim herein what I have claimed in my before-mentioned patent, No. 487,119, dated November 29, 1892.

It will be understood that the invention is not restricted to the precise numbers given in the foregoing description, nor to other details of the process, nor to apparatus, but that these are described by way of illustration and example.

I claim herein as my invention or discovery—

1. The process of removing the sulphur compound termed "skunk" from Canadian and similar petroleum, which consists in vaporizing the oil and subjecting the skunk-bearing vapors given off from the body of oil to the action in an undissolved condition of one or more of the oxides or oxygen salts of the metals of that class which are precipitated by hydrogen sulphide in acid solution and which form oxides soluble in skunk-bearing oil; substantially as described.

2. The process of removing the sulphur compound termed "skunk" from Canadian and similar petroleum, which consists in vaporizing the oil and subjecting the skunk-bearing vapors given off from the body of oil to the action in an undissolved condition of showers, films, or spray of one or more of the oxides or oxygen salts of the metals of that class which are precipitated by hydrogen sul-

phide in acid solution and which form oxides soluble in skunk-bearing oil; substantially as described.

3. The process of refining Canadian or similar skunk-bearing petroleum, which consists in vaporizing the oil and subjecting the skunk-bearing vapors given off from the body of oil to the action in an undissolved condition of one or more of the oxides or oxygen salts of the metals of that class which are precipitated by hydrogen sulphide in acid solution and which form oxides soluble in skunk-bearing oil, condensing the vapors from which the sulphur compound termed "skunk" has thus been removed, and washing the condensed liquid with sulphuric acid; substantially as described.

4. The process of removing the sulphur compound termed "skunk" from Canadian and similar petroleum, which consists in vaporizing the oil and subjecting the skunk-bearing vapors given off from the body of oil to the action in a dry state of one or more of the oxides or oxygen salts of the metals of that class which are precipitated by hydrogen sulphide in acid solution and which form oxides soluble in skunk-bearing oil; substantially as described.

In testimony whereof I have signed this specification in the presence of two witnesses.

HERMAN FRASCH.

Witnesses:
WM. A. EASTERDAY,
C. J. HEDRICK.