

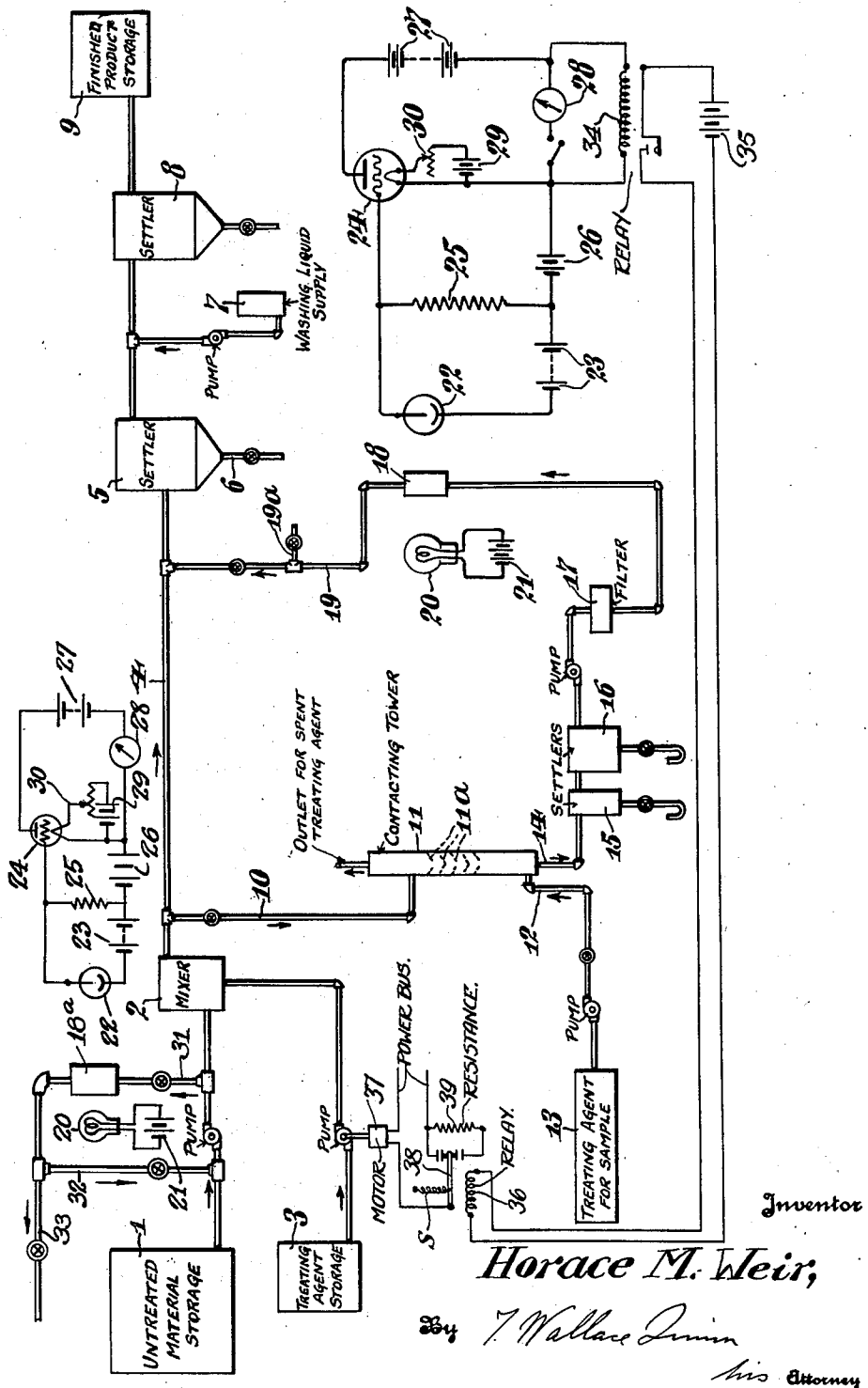
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PROCESS FOR CONTROLLING THE DECOLORIZING OF HYDROCARBON OILS

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PROCESS FOR CONTROLLING THE DECOLORIZING OF HYDROCARBON OILS

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The present invention relates to a process of and apparatus for recording the color of a liquid under treatment. It further relates to the control of processes by color measurement, and is especially adapted to the control of processes for color reduction of a liquid. As a specific aspect, the invention contemplates method and means for obtaining a record, and preferably a continuous record, of color of a liquid, as for example, petroleum oil, undergoing a decolorizing treatment, particularly a continuous decolorizing treatment, before and/or after the liquid is subjected to such treatment. The method and means whereby the invention may be carried out are hereinafter disclosed. The disclosure will suggest various applications and modifications of the process and apparatus to those skilled in the art, and these are considered within the scope of my invention.

While the invention is particularly adapted to the treatment of mineral oils generally, for convenience, it will be explained in connection with the acid treatment of lubricating stocks. It is to be understood, however, that my invention may be applied when decolorization of the oil is effected by means of other decolorizing agents, as for example, fuller's earth.

In view of the fact that mineral lubricating oils have been chosen as an example of liquid to be decolorized, a brief résumé of the usual processing and decolorization of such oils will be helpful to a better understanding of my control process as applied thereto.

In the refining of petroleum oil, the petroleum is separated into fractions, one or more of which may be classed as lubricating stock. However, as these oil fractions leave the still or fractionating column they are not suitable to be marketed in their then impure condition, but must be subjected to a further refining treatment which includes decolorizing.

While many methods may be employed for decolorizing these oils, a common method is to treat them with sulfuric acid. It is only desired, however, to reduce the color to a certain degree, and any further reduction of color is both undesirable and a waste of decolorizing agent. Therefore, it is desirable to control the amount of acid added as closely as possible to a particular amount. It is common practice to leave the addition of acid in charge of an operator who judges by eye the color of the treated oil, and either increases or decreases the amount of acid in accordance with such judgment. This method has many shortcomings, as may readily be sensed. The color of

oil produced will probably be as varied as the number of operators. Further, the oil will not be uniformly treated, sometimes being over-acidified, and other times being under-acidified. This comes from the fact that the operator may neglect controlling the acid for a period of time until he notices that the oil has, for example, been under-treated and is therefore too dark. Upon this notice he will most likely proceed to increase the flow of acid to make an oil of lighter color than the desired color of finished product, so that the blend of the two will result in the desired color. This requires much more acid than would be required if all of the oil had been uniformly treated, and further, it means that the color-imparting compounds which remain in the under-acidified portion which forms a part of the final oil product, are less desirable than the color-imparting compounds resulting from a correctly acidified or correctly treated oil.

The eliminate in a measure the shortcomings of this process, and also to serve other desirable purposes, I have provided as one specific aspect of my invention a process and apparatus for the continuous recording of the color of the oil both before and after acid treatment. The color of the oil before the acid treatment may be measured and recorded by passing a part of the oil stream between a source of light and a light sensitive body, for example, a photo-electric cell. Current through the photo-electric cell is made to operate an indicating and recording device. By these, together with additional steps, the color of the oil after acid treatment is similarly recorded.

In recording the color of the oil after acid treatment, it is not sufficient to merely measure the color of the oil after it has gone through the customary process. In such process the oil does not reach a finished condition until about 12 or 14 hours after the acid has been added, and consequently, measurement of the color at such time would not be useful in controlling the rate of addition of acid. In accordance with the need for quickly determining whether or not the correct amount of acid is being added, I have provided a process for quickly bringing a sample stream of the treated oil into suitable condition for color measurement, and automatically (by recording the color of the passing stream of oil) determining the insufficiency or the excess of the acid treatment, as the case may be.

The single figure in the drawing represents diagrammatically suitable specific apparatus in which my process may be applied to the acid treatment of mineral lubricating oil.

The process comprises continuously diverting a small portion of the stream of the acid-treated oil en route from the mixing chamber to the settling chamber, and passing the diverted sample into contact with gaseous ammonia, whereby the excess acid in the oil is neutralized. It is preferable, but not essential, to conduct the diverted stream of oil through a filtering medium of any suitable type to remove therefrom the acid sludge prior to neutralization. Any insoluble material present after the neutralizing is commonly removed before the stream of oil is subjected to color determination. A definite relationship which may be readily determined, exists between the color of the ammonia neutralized sample and the final color of the neutralized oil obtained as a finished product from the usual treating process. The sample obtained as above described is next passed through a glass sided cell, or its equivalent, which is interposed between a source of light and a light-sensitive cell, such as (1) a photo-electric or photolytic cell which includes an alkali metal cell, or (2) a selenium cell. The amount of light transmitted through the flowing stream of oil varies with the intensity of the color of the oil and accordingly with the degree of acid treatment, and will cause variations in the amount of (1) electric energy generated by the photo-electric or photolytic cell, or (2) resistance of the selenium cell, respectively. The rate at which electrical energy is generated in the photo-electric or photolytic cell or the changes which occur in the resistance of the selenium cell, as the case may be, is recorded on a scale or chart. The chart may, for example, be rotated under control of a clock mechanism and color may be recorded by transverse fluctuations of a recording point.

Making particular reference to the single figure in the drawing, a detailed description of one method of carrying out my process, applied to the treatment of mineral lubricating oil, will be disclosed.

Oil which is to be acid treated, for instance, oil from one or more plates of a fractionating column of a pipe still distillation system, is pumped from source of supply 1 to the knothole mixer 2 where it is intimately mixed with a continuous stream of acid from tank 3.

In passing from source of supply 1 to the mixer 2 a sample stream of the untreated oil is diverted through valve controlled line 31, and is passed through a transparent tube 18a for observation or color testing (as for example, by a system including elements numbered in the drawing as 20 to 30, which hereinafter will be described in detail), and thence is either introduced back into the main stream of oil through valve controlled line 32, or, if desired, it may be passed to a suitable receptacle (not shown) by means of valve controlled line 33. In passing through the transparent tube 18a the color intensity of the sample stream of undecolorized oil is measured and recorded, for example, by means hereinafter referred to and shown in the drawing in connection with transparent tube 18.

The oil-acid mixture is transferred from the knothole mixer through line 4 to a settling tank 5. Acid sludge is withdrawn through line 6 located at the bottom of the settling tank. Oil is transferred from adjacent the top of the tank 5, and after being mixed with water from tank 7 is resettled in the water settler 8, and then is pumped to suitable storage 9. A continuous sample is diverted from line 4 by means of valve-controlled line 10 which leads to the upper portion of ammonia contacting tower 11 which contains baffles, packing or other liquid-vapor contacting means 11a. The oil flows downwardly through this tower countercurrent to and in direct contact with gaseous ammonia which is introduced into the lower portion of the tower through line 12, which leads from an ammonia supply in tank 13. In traveling through the tower, the oil is neutralized and the mixture of oil and acid sludge passes from the bottom of the tower through line 14 into settlers 15 and 16. The oil freed from sludge in the settlers 15 and 16, is passed from the latter into and through a sand filter 17.

The color of the oil coming from the sand filter, while it may not necessarily be the same as that of the oil passing to tank 9, does bear a definite relationship to the color of the finished oil, and a variation in color of the diverted stream of oil after treatment as aforesaid from a fixed standard of comparison at once indicates that an incorrect amount of acid is being admixed with the oil.

After passing through the filter 17 the diverted stream of oil is passed through a transparent tube 18 which is interposed between incandescent lamp 20, connected with battery 21, and light sensitive cell 22. The oil after passage through tube 18 may be returned to line 4 through valve controlled line 19, or if desired since the stream of diverted oil is small, it may be conveniently collected in a suitable vessel by passing it from the system through valve-controlled line 19a which taps line 19.

The light sensitive cell 22 comprising a photo-electric cell upon which is impressed a constant voltage from source 23, is connected to the grid and the cathode of a vacuum tube 24. Between the grid and the cathode of this vacuum tube is connected a resistance 25. Interposed between this resistance and the cathode of the vacuum tube is the biasing battery 26. The anode of this vacuum tube has impressed upon it a constant voltage from source 27, and the cathode is heated by current from supply source 29, the constant electromotive force of which is adjusted by rheostat 30. As will be seen, the anode current and therefore the color of the oil passing through tube 18 is indicated and/or recorded by a galvanometer or potentiometer 28. The scale of this indicating instrument is adjusted so that color of the finished product will be indicated, for instance, in the center of the scale, as at zero, and variation from this desired color may be indicated and recorded as a positive or negative number depending upon whether the oil is higher or lower in color than desired.

In operation, the diverted stream of acid-oil mixture is quickly neutralized, settled, filtered and passed through the transparent cell, so that variation in the amount of acid from that required to produce a fixed standard is indicated continuously and within a short period of time. Having determined the relationship between the scale reading and the desired color of the finished oil leaving the settling chamber, it is seen that a direct check on the sufficiency or insufficiency of the acid treatment is had, and this within a very short time, which may be of the order of 3 minutes after the oil has been treated, and before enough time has elapsed for any substantial change in the condition of the oil, acid, or operating of the apparatus to occur.

If it is desired to regulate the decolorizing treatment in an automatic manner, a system of relays may be employed in conjunction with the photo-electric circuit. For example, a sensitive

relay 34 may be placed in the photo-electric circuit in place of the galvanometer 28, such relay being in series with a battery 35, and a second relay 36 adapted to handle the current necessary to energize the pump motor 37. Should the sample stream of oil flowing thru the tube 18 be undesirably light in color, the intensity of the light passing thru the oil in the tube will be sufficient to cause a considerable flow of current in the photo-electric circuit, and such current will energize the sensitive relay 34 to close the circuit including the battery 35 and the relay 36. Relay 36, thus energized, will bring the relay contact bar 38 into the lower position, thus closing the pump motor circuit including the resistance 39. The increased resistance in the pump motor circuit will cause the pump motor to slow down and less treating agent will be introduced into the mixing vessel 2, in contact with the oil to be treated. On the other hand, if the sample stream of oil passing thru the tube 18 is undesirably dark in color, little light will be transmitted therethru, and little current will flow thru the photo-electric circuit. As a result, the relay 34 will not be energized, nor will the relay 36, and the contact bar 38 will be held in the upper position by spring S, closing the pump motor circuit, resistance 39 being out of said circuit. The pump motor will then increase in speed and the pump will deliver a greater quantity of treating agent to the mixing vessel 2.

The method herein employed in expressing color of liquids is based on a definition of color similar to the concept of concentration of solutions. Thus a suitable standard liquid is arbitrarily assigned a standard color figure, say 10. By definition the color which results from mixing S volumes of the standard liquid with W volumes of a colorless white liquid, is taken as

$$\frac{S}{S+W} \times 10.$$

The colorimetric scale is so arranged that this concept of color concentration, or color intensity, as it is more generally designated, is retained over the whole range of colors, from the darkest liquid to a colorless liquid itself. As can be seen, this system of expressing color provides a simple mathematical relationship between readings, the "black" undecolorized distillate having its color intensity expressed in the same units as those used to express the color of highly refined products. Further elaboration upon this method of expressing colors will be found in Vol. 22 (1930) Industrial and Engineering Chemistry, page 1293, et seq., in an article entitled "The acid treatment of lubricating distillates", by W. F. Houghton, F. M. Majewski and myself.

However, the matter of quickly determining the color of the oil after acid treatment is the feature of greatest significance, and the matter of making the control entirely automatic is a feature of the invention which may or may not be employed, as desired. It can be readily sensed that time is of the essence in arriving at this color determination, for the longer the period of time which elapses between the time of addition of the acid and the time at which the sufficiency or insufficiency of acid treatment is determined and communicated to the acid inlet valve, the greater will be the fluctuation of acid treatment, both under and over the correct amount.

While the measurement of color after acid treatment is normally the only essential meas-

urement in accomplishing certain aforementioned objects of my invention, e. g., controlling the rate at which acid is added to the undecolorized oil, yet by combining therewith the measurement of the color before acid treatment, that is, for example, after the oil leaves the fractionating column and before it is introduced into the mixing chamber, the degree of color reduction which actually takes place can be measured and recorded. For example, by having this record both before and after acid treatment, the inefficient operation of the oil-acid mixing device could be discovered or a possible deterioration in strength of the acid could be located. Also, it will be seen that the process serves as a check on the operator, where changes are to be communicated from the light sensitive cell to the acid inlet valve manually. Accordingly, it serves to increase the economy of the process by making the acid treatment uniform, for, without this continuous record or the equivalent, there would be no way of knowing whether the operator treated uniformly, or not. In addition the record of color before acid treatment serves to indicate the regularity or irregularity of operation in the fractionating column or other equipment through which the oil passes prior to the acid treatment. For example, improper deentrainment of liquid from the vapors in the operation of a fractionating column would manifest itself by an increase in color intensity of the oil issuing from one or more of the side streams from the column.

In saying that uniform treatment will make for economy in acid consumption it might be well to point out that more acid is required per unit of color reduction below the desired color standard than is required per unit of color reduction above the desired standard. That is, when one tries to reduce the last traces of color from an oil a large excess of acid must be used. The amount of acid actually consumed in removing certain quantities of color imparting compounds from an oil of low color intensity is necessarily much greater than the amount of acid which would be consumed in removing a corresponding amount of color-imparting compounds from an oil of higher color intensity.

The rotation of the color recording charts in the preferred arrangement of my apparatus is controlled by a clock mechanism, so that the color intensity of the incoming oil and the outgoing oil at a particular time can be ascertained. If, for example, the oil before treatment runs quite uniform in color, and the color record of the treated oil is shown by a line having a large number of fluctuations both above and below the standard color datum line, it is indicative of poor control on the part of the operator. However, if records both before and after treatment are quite uniform or free from any large fluctuations, and yet an abnormally large amount of acid was consumed, it is indicative of some irregularity in the performance of the equipment, strength of acid, and/or prior treatment of the oil.

From the foregoing it will be understood when in the appended claims a process or means for supplying an "economic control" is spoken of, that economic control comprehends elimination of the excessive use of acid or other decolorizing agent, control of the efficient functioning of the apparatus and equipment, and ascertainment of unfavorable conditions which may exist in the treatment given the oil prior to the decolorizing treatment.

While I have described my invention with particularity, it will be understood that it broadly relates to a process for the controlled decolorization of hydrocarbon oils. Regardless of the specific decolorization process or means used, e. g., regardless of whether acid or other decolorizing agent is employed in the decolorization, it is to be understood that it is within the scope of my invention to efficiently control in such decolorizing process. Further, it will be observed that in the treatment of the diverted sample stream, as disclosed, the steps in the process of bringing the sample stream into a suitable condition to have its color measured may be varied within limits, and still permit a record to be had which will bear a substantially direct relationship to the final color of the main body of the oil being treated. The essential thing is to choose such steps for bringing the oil being treated to a condition where its color may be determined, that will require a minimum of time to intervene between the addition of acid or other decolorizing agent and the determination of the sufficiency or insufficiency of the amount of such agent being added.

While a light sensitive cell or similar device is given herein as a means for automatically determining the color of the treated oil, it is also possible, though less satisfactory, to determine with the eye in a modification of an ordinary colorimeter the color of the stream of neutralized oil by comparison with a standard sample.

It is pointed out that a combined process of decolorization control including the step of recording color of the passing oil before treatment is distinctly advantageous. The idea of variation in color of a black oil issuing from the fractionating column was entirely overlooked prior to my invention. This oversight may be explained by the fact that the oil as it issued from the fractionating column always appears black even though, as my co-workers and I have determined, its color intensity does vary within wide limits. Thus it is really a variation in color intensity which is to be recorded, in accordance with my invention. This process of color recording has meant a great saving in acid. The continuous

color record serves to keep a constant check on whether or not a fractionating column is efficiently functioning to eliminate entrainment, and to locate other places in the treating process and apparatus in which improvement can be made.

What I claim is:

1. The process of controlling the decolorizing treatment of hydrocarbon oil by passing through a conduit a stream of said oil to which a decolorizing acid has been added, diverting a relatively small sample stream of oil from said main stream, introducing a measured quantity of a neutralizing agent into said sample stream, adapted to quickly react with said sample stream and impart a color intensity thereto bearing a predetermined relationship to the ultimate color of the acid-treated oil flowing in the main stream, clarifying the oil in the sample stream by the removal of sediment therefrom, photoelectrically recording variations in the color intensity of the clarified oil in said sample stream, photoelectrically recording variations in color intensity of the oil in the main stream prior to acidification and comparing said records as a means for controlling the decolorizing operation.

2. The process of controlling the decolorizing treatment of hydrocarbon oil by passing through a conduit a stream of said oil to which a definite quantity of sulphuric acid has been added, diverting a relatively small sample stream of oil from said main stream, introducing a measured quantity of ammonia into said sample stream adapted to quickly react with said sample stream and impart a color intensity thereto bearing a predetermined relationship to the ultimate color of the acid-treated oil flowing in the main stream, clarifying the oil in the sample stream by the removal of sediment therefrom, photoelectrically recording variations in the color intensity of the clarified oil in said sample stream, photoelectrically recording variations in color intensity of the oil in the main stream prior to acidification and comparing said records as a means for controlling the decolorizing operation.

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