Nov. 6, 1962 A. DOUTY 3,062,963

METHOD OF MONITORING COLORED FLUIDS

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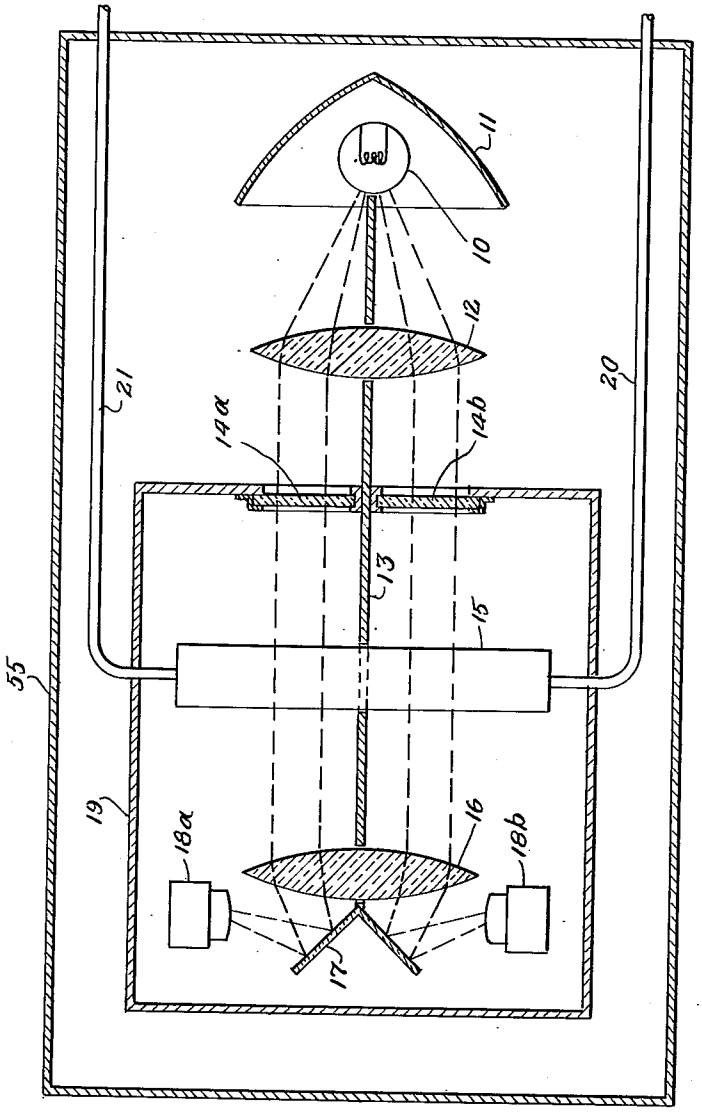


Fig. 1.

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Fig. 2.

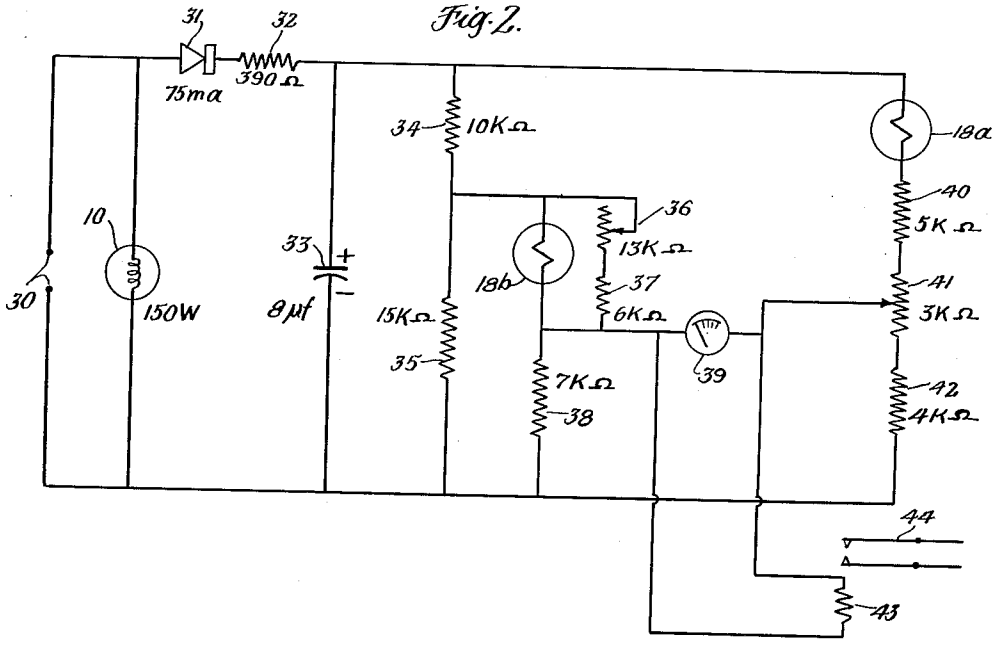
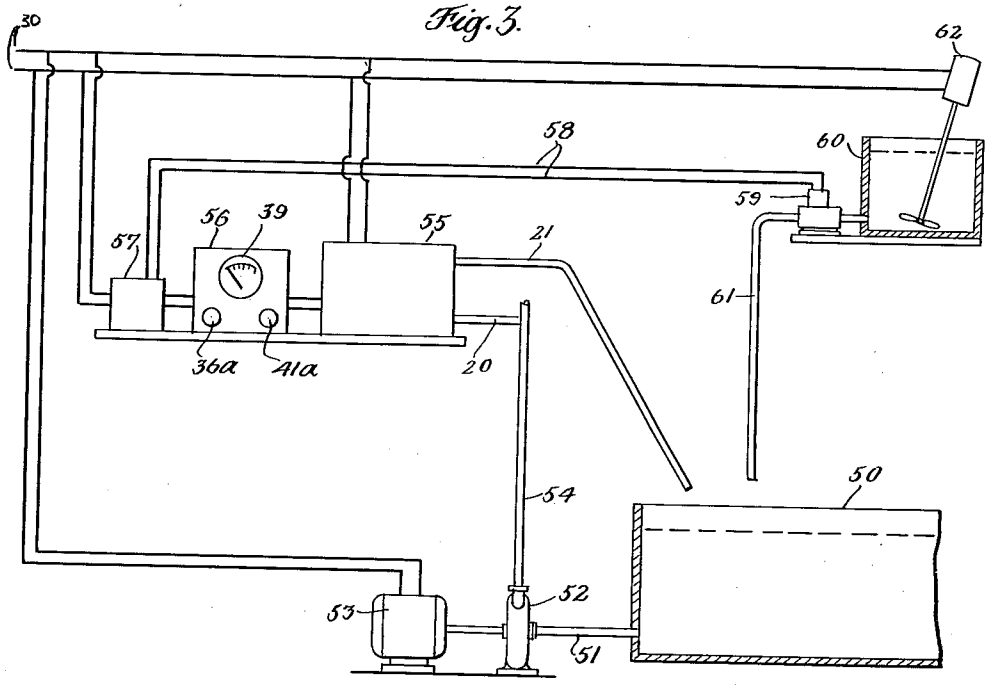


Fig. 3.



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METHOD OF MONITORING COLORED FLUIDS

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This invention relates to a method and apparatus for monitoring the composition of fluids by utilizing certain optical properties of components of the fluid under consideration. As used herein, the term "light" includes electromagnetic radiation in the visible range, in the ultraviolet range, and in the infra-red range. The method and apparatus has been found to be particularly useful in monitoring liquid solutions containing a colored component, the concentration of which is important, together with other components which are colored in the sense that they absorb or scatter light.

Many industrial fluids, especially liquid solutions, contain as one of the key components a colored substance. The concentration of this colored substance is often of great importance in the utilization of the fluid or liquid solution, but because of other substances present in the solution the concentration is difficult to monitor. Since the light absorption of a colored constituent or component of a solution varies with the concentration of that component according to well-known laws, one possible method of monitoring the concentration would be to measure the light absorbence of the solution, by passing light through a selected thickness of the solution.

Such a straight forward approach is impractical in many industrial solutions because in addition to the key colored substance whose concentration is of primary interest the solutions contain other colored substances which for present purposes may be generally designated as "impurities." The concentration, color, and light absorption properties of such impurities may vary independently of the concentration of the key colored substance, or if not independently, may be related to the concentration of the key colored substance in such a complex manner as to defy analysis.

The method and apparatus of my invention are based on several important discoveries concerning the light absorption properties of solutions containing a key colored substance together with colored impurities. While these discoveries were made in the study of a single type of industrial solution, namely acid solutions containing hexavalent chromium together with various other constituents for the treatment of aluminum surfaces (and will hereinafter be discussed in detail in the context of such solutions) the underlying principles may be stated generally and are applicable to many solutions. Consider first the key colored substance whose concentration is to be monitored. In many cases it will be found that such a substance in a solution will cause reproducible absorption of light of a given wave length or narrow range of wave lengths. However, at another wave length or narrow range of wave lengths the key colored substance may have a very low absorbence for light. When the very low absorbence in this second spectral region is compared with the absorption response of the substance to light in the first spectral region, the response in the second region may very well be so low as to be negligible.

Considering now the colored impurities, it has been discovered that for many classes of impurities the absorption of light remains fairly constant over a wide range of wave lengths. In particular, the absorption by a given type and concentration of colored impurities at the wave length for which the key colored substance is appreciably and reproducibly absorbed, is not far different from the absorption by the impurities at the wave length where the key colored substance has little or no absorbence.

These discoveries provide the basis for my invention, in which the light absorbence of a sample is measured at a wave length of light which is materially absorbed both by the impurities and by the key colored substance, and also at a wave length of light which is absorbed only by the impurities. A comparison of the absorbences has been found to yield a reliable measurement of the concentration of the key colored substance.

In my invention the above comparison of absorbences is accomplished electrically. Therefore, there may be provided certain well-known types of control apparatus which respond to an electric signal. This apparatus may be used to control mechanical equipment for the adjustment of the concentration of the solution being tested. The adjustment usually consists of adding material in either solid or liquid form to the solution.

It is an object of this invention to provide a method and apparatus for monitoring the concentration of a colored substance in a fluid which contains other colored substances.

It is a further object of this invention to provide a method and apparatus for maintaining the concentration of a colored constituent of a fluid at the desired level when the fluid is used in such a way as to more or less continuously tend to alter the concentration of the colored constituent.

Another object of this invention is to provide means for measuring the concentration of a colored substance in a fluid in the presence of other colored substances, which other colored substances may vary in color and concentration independently of the concentration of the substance being measured.

Still another object of my invention is to provide a method and apparatus for monitoring the concentration of a colored substance in a fluid continuously and without degradation of the sample used for measurement purposes.

An important object of my invention is to provide a method and apparatus for monitoring the concentration of hexavalent chromium in solutions for treating the surfaces of aluminum and aluminum alloys, which solutions contain as an important ingredient acid hexavalent chromium together with other substances. These objects, together with other objects and purposes, may be more clearly understood by considering the following description and drawings in which:

FIGURE 1 illustrates more or less diagramatically one form of the optical portion of apparatus which I have found useful in monitoring aluminum treating solutions;

FIGURE 2 is a wiring diagram showing a circuit involving photoelectric devices, which I have found useful in measuring the concentration of hexavalent chrominum in aluminum treating solutions; and

FIGURE 3 is a diagramatic illustration of the application of my monitoring and control equipment to the working solution in an industrial installation.

Inasmuch as my invention is particularly applicable to aluminum coating solutions, this detailed description will be directed principally to the problems involved in such solutions and the manner in which they are met by my invention.

In the art of applying corrosion protective and decorative coatings to the surfaces of aluminum and aluminum alloys, several well-known processes include, as an essential step, treatment of the surfaces with acid aqueous solutions containing hexavalent chromium together with other substances. Examples of such a process may be found in U.S. Patent Nos. 2,438,877; 2,471,909; 2,472,-864; 2,563,431; and 2,796,370. Although the operation of such processes is flexible, the common practice in mass production type operations is to employ a working solution which is sprayed upon a succession of aluminum

objects or into which a succession of aluminum objects are dipped. Each aluminum object, of course, uses up some of the hexavalent chromium and the other active constituents, thus leaving the working solution weaker in active coinstituents after a given object has been treated than it was before that object was treated. In addition, the working solution will contain, after the treatment of a given object, reaction products, in particular trivalent chromium, aluminum, and solid suspended matter derived from the aluminum alloys being treated. The concentration of these "impurities" in the working solution will increase as each succeeding aluminum article is treated.

The quality of a protective coating formed on the aluminum by such a process is strongly dependent on the concentration of the active constituents, especially hexavalent chromium, in the working solution. Inasmuch as uniformity from article to article is a general requirement in mass production industries, it is highly desirable to maintain the concentration of the hexavalent chromium and the other active constituents of the working solution by more or less constant addition of fresh material to the working solution.

The characteristic color of hexavalent chromium in an acid solution is bright orange. The chromium ions have been found to exhibit appreciable light absorbence for light of wave lengths in the range from near ultraviolet up to at least 550 millimicrons. This absorption is strongly responsive to concentration in a predictable way. However, it has been discovered that at light wave lengths of 600 millimicrons and further into the red end of the spectrum hexavalent chromium exhibits essentially zero absorbence. The impurities which are common in the working solutions used in aluminum treating have been found to exhibit strong light absorbence through a wide range of the spectrum, that is from near ultraviolet up to and beyond 650 millimicrons and on into the infra-red range. The absorbence of these impurities, if they are present in a material amount, so overshadows the absorbence attributable to the hexavalent chromium that a single or "gross" absorbence measurement made on a working solution would be useless as a measurement of the hexavalent chromium concentration. However, further discovery was made that the light absorbence of the impurities (at a given concentration) at 600 millimicrons and further into the red end of the spectrum was not greatly different from the absorbence of the impurities at lower wave lengths, for example, 500 millimicrons. Thus, by measuring the light absorbence of a working solution containing hexavalent chromium and impurities at 500 millimicrons, thereby obtaining an absorbence attributable to both the chromium and the impurities; and separately measuring the light absorbence of the working solution at 600 millimicrons, thereby obtaining a light absorbence attributable to the impurities alone, and comparing these two absorbences, an absorbence attributable to the hexavalent chromium alone may be obtained by difference. From this the concentration of hexavalent chromium may be obtained by the application of well-known physical laws.

It should be noted that the discovery discussed above (the light absorbence of the impurities at a given concentration being approximately the same at 600 millimicrons and at 500 millimicrons) involves a further subsidiary discovery which is also important to the operation of this invention. This discovery is that, for many types of impurities, the relation between the concentration of impurities and the light absorption is approximately the same at the two wave lengths involved.

Throughout the above description the terms "absorbence" and "absorption" have been used in a broad sense to include both absorption in its rigorous sense, that is, where the energy in the light waves is actually absorbed by the ions or particles and absorption in a sense which is more mechanical in nature and which might more properly be called scattering or back scattering.

Referring now to FIGURE 1 which illustrates the physical arrangement of the optical portion of the apparatus that I have found useful in monitoring aluminum treating solutions, it can be seen that there is provided a light source **10** which is preferably in the form of a concentrated filament incandescent lamp. Arranged adjacent to the lamp **10** is a parabolic reflector **11**. Light passes from the lamp through the condensing lens **12** which renders it substantially parallel. The light from the lamp **10** is segregated into two separate beams by means of the baffles **13** whose arrangement will be discussed in more detail below. The light in the upper beam after being rendered parallel by the lens **12** passes through the filter **14***a* which filters out the light of all wave lengths except the selected band of wave lengths. In the embodiment arranged to monitor aluminum treating solutions the selected band of wave lengths passed by the filter **14***a* is in the region of 600 millimicrons. A suitable filter for this purpose has been found to be an interference filter made by the Bausch & Lomb Optical Company passing light with a band width of about 5 millimicrons. Similarly, light in the lower beam after being rendered parallel is passed through the filter **14***b* which passes only light in the region of 510 millimicrons. An interference filter of the same type made by the Bausch & Lomb Optical Company is satisfactory for this application also.

The means which may be used for isolating the narrow spectral regions referred to herein include any of the usual known types of optical filter. If extremely narrow bands of wave lengths are necessary, any form of monochromator, based either on prisms or diffraction gratings, may be employed. Since such devices are comparatively expensive, optical filters are to be preferred over them if they are at all suitable.

The upper and lower beams after passing through the filter are passed separately through the absorption cell **15** which contains the fluid being monitored. This absorption cell will be discussed in more detail below. The light in each beam is then passed through a second lens **16** which directs it on to the mirror structure **17**. It can be seen that the mirror structure **17** is made up of two plane mirrors mounted at right angles to each other, each being at 45° to the general axis of movement of light through the apparatus. The light in the upper beam is thus reflected onto the light receiving surface of the photocell **18***a* while the light in the lower beam is similarly reflected onto the light receiving surface of the photocell **18***b*.

It should be noted that the absorption cell **15**, the lens **16**, the mirror structure **17**, and the photocells **18***a* and **18***b* are all located within the light-tight housing **19**. The baffles **13** which serve to maintain the upper and lower beams separately from each other run substantially from the lamp **10** to the mirror structure **17**. They are interrupted or pierced only by those elements which are common to both the upper and lower beam, that is, the lenses **12** and **16** and the absorption cell **15**. In this way there is permitted only a minimum of mixing between the two beams, even though both beams pass through certain components of the system. If desired, even more complete separation of the two beams may be obtained by utilizing separate condensing lenses **12** and **16** and separate absorption cells **15** for each beam.

The absorption cell **15** is constructed of material which is essentially transparent to the radiation at both of the wave lengths involved and is necessarily constructed of material which will resist the corrosive nature of any fluid being tested. The absorption cells which have been found satisfactory in apparatus used to monitor aluminum treating solutions are made of transparent plastic, for example poly (methy methylacrylate). The cell is

provided with an inlet tube 20 and an outlet tube 21 which are connected to apparatus that will be discussed later for providing a continuous flow of test fluid through the cell. The walls of the absorption cell are preferably arranged to lie essentially transverse the axis of the light beams. The thickness of the liquid sample, which is established by the spacing of the opposite walls of the absorption cell, may be chosen within rather wide limits determined primarily by the character of the solution or fluid being tested. For example, in very old and highly contaminated solutions (the contamination being colored impurities) a thin cell with a sample thickness of as little as 2 millimeters may be used. For solutions which have a lower level of contamination, cells with a sample thickness of a centimeter or more may be employed.

The photocells 18*a* and 18*b* may be of any type suitably sensitive to light of the wave lengths employed. In one useful embodiment of the apparatus, I have found that R.C.A. photocell type No. 6957 has proven quite satisfactory for each of the photocells.

It will be realized that other arrangements of the basic physical parts of my apparatus are possible. In particular, the filters 14*a* and 14*b* may be positioned so that the light is filtered after its passage through the absorption cell 15 but before it strikes the photocells 18*a* and 18*b*. This arrangement of the equipment may be of advantage if the filters employed are heat sensitive, because the test fluid flowing through the absorption cell will absorb some of the infra-red radiation from the light source, thus protecting the filters from heat damage.

A suitable electric circuit for utilizing the differential output of the two photocells to operate control equipment is shown in the wiring diagram of FIGURE 2. Indicated on the diagram are nominal values for the resistors and various other components which have been found to be satisfactory in apparatus utilizing the above mentioned photocells to monitor hexavalent chromium solutions. These values are to be taken as illustrative only, and not as limiting. Alternating current is supplied at 30 and is utilized as received to operate the light source 10. The current from the lines is rectified by the half-wave rectifier 31 and passed through the current limiting resistor 32. It is then filtered by the condenser 33. The rectified voltage is then supplied to the voltage bridge containing the photocells 18*a* and 18*b* together with the various resistors shown in the drawing. The voltage placed across the leg of the bridge containing the photocell 18*b* is lower than the voltage placed across the photocell 18*a*, the reduction being accomplished by means of the bleeder circuit including the resistors 34 and 35. In the unit used for monitoring aluminum treating solutions, the voltage at the top of the photocell 18*b* is approximately 63 volts and the voltage at the top of the photocell 18*a* is approximately 105 volts. This imbalance of supplied voltage to the legs of the bridge is desirable because the current output of the photocell 18*b* is more strongly affected by light of 510 millimicrons falling upon it than is the current output of the photocell 18*a* caused by light of 600 millimicrons falling on it.

The photocell 18*b* is shunted with the variable potentiometer 36 and the resistor 37. The remainder of the bridge leg for the photocell 18*b* includes the series resistor 38. One side of the voltmeter 39 is connected to the leg of the bridge containing the photocell 18*b* below the photocell and the shunt circuit and above the resistor 38.

The leg of the bridge containing the photocell 18*a* includes the resistor 40 in series with the photocell and the potentiometer 41, the variable portion of which is connected to the other side of the voltmeter 39. The lower portion of the leg of the bridge containing the photocell 18*a* includes the resistor 42.

By means of this bridge circuit, the response of the voltmeter can be made approximately linear with the concentration of hexavalant chromium in the solution being tested. This is a great advantage for indicating purposes and for utilization of the voltage developed at the voltmeter to operate proportional controlling apparatus. The exact character of the response of the voltage developed at the voltmeter with respect to the concentration of hexavalent chromium is less important if this voltage is to be utilized to operate on-off control equipment calibrated to maintain a pre-selected concentration in the working solution.

The voltmeter may be calibrated to give a reading of zero by filling the sample cell with pure or distilled water and adjusting the potentiometer 41 until the meter reads at zero. Changes in the character of the impurities, for example a relative increase in the concentration of impurities of a given color, may be compensated for by adjusting the potentiometer 36.

In FIGURE 2 the voltmeter is shown as being shunted by the coil of a control relay 43 which is polarized to pull in at pre-selected readings of the voltmeter. This relay closes the switch 44 thereby energizing equipment for adding hexavalent chromium to the working solution. A satisfactory type of relay for this purpose is a meter relay consisting of a voltmeter with an internal slave relay included in it. Such meter relays are commercially available and are well suited both as indicating devices and controllers for the feed apparatus. Meter relays of this type often include a timer switch mechanism within them which causes the relay to remain closed or open for a selected fixed interval depending on the position of the meter needle at the beginning of each such fixed interval. In this way the operation of the feeding apparatus is damped, thereby eliminating chattering of the valves, "hunting," or resonant cycling. A wide range of timing intervals is available if such equipment is used. For example, intervals of 15 seconds to 15 minutes have been found satisfactory depending on the needs of the system. The voltage developed across the voltmeter 39 may be fed into a self-balancing potentiometer-recorder-controller instead of the simpler on-off relay control shown in FIGURE 2. If this is done the apparatus will be capable of proportional control instead of on-off control. Such self-balancing potentiometer-recorder-controllers are well known in the art and will not be discussed here in any detail.

In FIGURE 3 the equipment of my invention is shown as applied to an industrial installation for aluminum treating. For simplicity only those parts of the treating system which are necessary in the operation of my invention are shown. The working solution is held in the tank 50. The line 51 runs from the tank to a pump 52 driven by the electric motor 53. The pump 52 forces the working solution up the riser to spray nozzles (not shown) through which the working solution is sprayed onto the aluminum surfaces (also not shown) which are being treated. The working solution after contacting the aluminum falls back into the tank 50.

The optical equipment illustrated in detail in FIGURE 1 is enclosed in the housing 55. It should be noted that within the housing 55 there is a light-tight housing 19 discussed earlier in connection with FIGURE 1. A portion of the working solution moving through the riser 54 is drawn off through the inlet tube 20 which conducts it into the absorption cell 15 within the housing 55. The outlet tube 21 conducts the fluid from the absorption cell back into the tank 50. With the exception of the photocells 18*a* and 18*b*, and the light 10, the electrical components shown in FIGURE 2 are located in the housing 56. In actual practice, of course, the housings 55 and 56 may be combined. The dial of the voltmeter 39 is mounted on the face of the housing 56. The knob 36*a* permits adjustment of the potentiometer 36. Similarly, the knob 41*a* permits adjustment of the potentiometer 41. The control relay 43 (on FIGURE 2) is

shown as being located in a separate housing 57 on FIGURE 3. However, it will be remembered that this control relay may be an integral part of a commercially available meter relay. The control relay located within housing 57 is connected by the electric lines 58 to the solenoid 59, which operates a valve admitting fresh hexavalent chromium solution from the replenishing tank 60 through the line 61 into the working solution tank 50. The replenishing tank is shown equipped with a mixer unit 62 for pre-dissolving the solid chemicals.

Alternating current is supplied at 30 through various lines to the motor 53, to the electrical elements located in the housings 55, 56, and 57, and to the mixer 62.

My invention admits of considerable flexibility in the arrangement of the mechanical portions of the control system. For example, if the physical arrangement of the installation requires that the replenishing tank 60 be located below the level of the working solution tank 50, the solenoid 59 and its attendant valve may be replaced by a pump driven by an electric motor which is controlled by the relay contained in the housing 57. If it is desired to add the replenishing materials in dry or powdered form, the replenishing tank 60 and the solenoid 59 and its valve may be replaced by a conveyor feeder which is turned off and on by the monitoring apparatus, thus feeding directly into the working solution tank 50 or into a pre-dissolving tank. If a self-balancing potentiometer-recorder-controller is employed instead of a simple on-off relay, it may be used to actuate, by the usual pneumatic or electric means, the degree of opening of a proportioning valve in line 61 running from the replenishing tank 60.

This general arrangement of the equipment of my invention will automatically maintain the proper level of the colored constituent, in the case of aluminum treating solutions hexavalent chromium, in the working solution. This in itself is an important advantage. However, it will be remembered that the working solution generally contains other active and important constituents. In many cases the rate at which these other constituents of the working solution are exhausted is related to the rate at which hexavalent chromium is exhausted. Therefore, the replenishing solution in the tank 60 may be formulated in such a way that the addition of enough of that solution to the working solution to restore the proper concentration of hexavalent chromium will also result in the addition of the proper amounts of the other active constituents. Thus, monitoring of the concentration of hexavalent chromium can serve as a controlling means for all of the active ingredients.

Although my invention has been described in detail with respect to its application to aluminum treating solutions containing hexavalent chromium together with impurities, it is applicable in many other situations. By way of summary, the general conditions which determine the applicability of my invention are as follows: (1) the ingredient which is to be monitored and controlled must cause the reproducible absorption or scattering of light in the fluid involved and its relative absorbence for light of a first wave length must be quite low when compared to its absorbence for light of a second wave length; (2) the absorbence for light of the controlled ingredient should be strongly dependent on the concentration of that ingredient at the second wave length; (3) other substances ("impurities") which occur in the fluid involved may exhibit substantial absorbence for light of both the first wave length and the second wave length. However, the magnitude of the absorbence caused by the impurities at a given concentration must be approximately the same for light at either wave length and the effect of concentration of the impurities on the absorbence must be similar at both wave lengths. Once these conditions are met, the problem is reduced to the selection, by those skilled in the art, of the proper physical components to make the required measurements. These problems involve the selection of photocells of sufficient sensitivity to the wave lengths of light selected, selection of suitable optical filters for creating light of the chosen wave lengths, and the construction of absorption cells which are transparent to the light at the wave lengths involved.

For brevity of description several terms are used in the appended claims in a rather broad sense. These terms are defined as follows:

"Light" means electromagnetic radiation of wave lengths included in the ultra-violet, visible, and infra-red regions.

"Colored" means having a non-uniform transmittance for light (as defined above) of various frequencies (or wave lengths) when the substance is dissolved or suspended in a fluid.

"Filter" means a device passing light of a narrow band of wave lengths and includes optical filters and monochromators.

"Absorption cell" means a vessel for the fluid transparent to the light of the wave length range it is desired to measure.

"Photoelectric device" means a photocell or other device in which incident light causes a potential difference across the device or an increase in current through the device.

I claim:

A method of monitoring hexavalent chromium in aluminum treating solutions containing varying amounts of other colored substances including varying amounts of trivalent chromium, which method comprises directing a first beam of light of a narrow band of wave lengths in the region of 510 millimicrons through a fixed thickness of said aluminum treating solution, directing a second beam of light of a narrow band of wave lengths in the region of 600 millimicrons through said fixed thickness of aluminum treating solution, directing said first and second beams of light, after their passage through the aluminum treating solution, onto photoelectric means electrically responsive to the quantity of light falling thereon, and comparing the electrical response of said photoelectric means caused by the relative quantities of light in said first and second beams, whereby to obtain a measurement of hexavalent chromium concentration in said solution.

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