46

# ADVANCES IN SOLVENT-DEWAXING OF MINERAL OILS AND TARS

By Dr. Karl A. Fischer

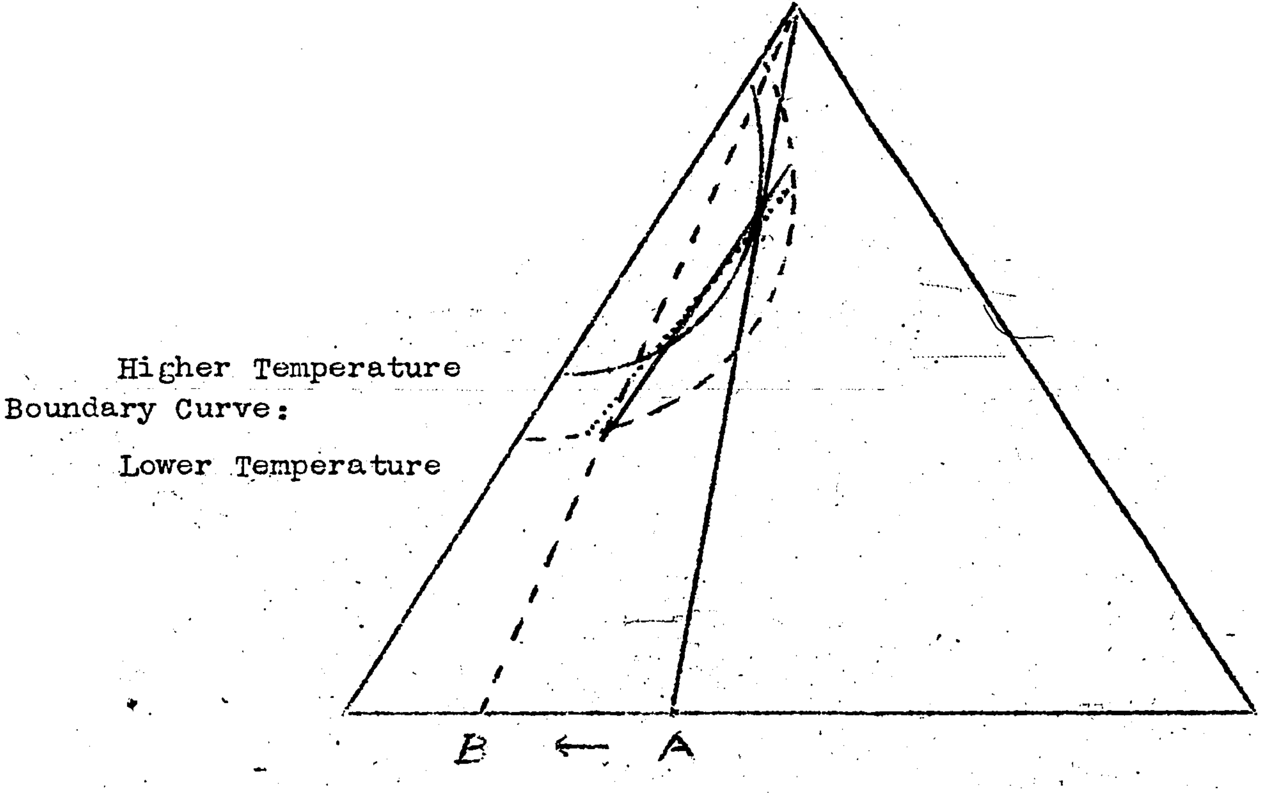
## ARTICLE VI

## TECHNICAL VIEW POINTS, OTHER DEWAXING IDEAS, MISCELLANEOUS

# ARTICLE VI

## TECHNICAL VIEW POINTS

From the theoretical considerations presented in previous articles, we can derive some practical points of view, which are of the greatest importance for good plant operation. It is the phase problem which determines fundamentally whether or not our final products will be satisfactory and this consideration shall range first. Optimum results can only be expected if operating conditions come close to the field of phase separation and all determining factors must then be closely watched. Those factors are a) temperature, b) dilution and c) selectivity of the solvent. Selectivity is adjusted by the blending ratio of the solvent components. Any small deviation of either one of those three figures will cause a disadvantageous effect. That is why the heart of each dewaxing plant is its regulating and recording instrument controls for a) temperature in chilling, b) concentration in diluting and c) specific gravity for adjusting solvent blending ratio. Smooth operation demands furthermore regulation and recording of oil intake, predilution and quantity of wash liquid. Those automatic regulators must be absolutely dependable. Regulation of those items by hand and according to gauge readings will never satisfy the technical demands. More regulators for temperature and pressure in evaporation of filtrate and wax cake as well as for levels are desirable but great care must be taken to avoid retroaction of regulators which become dependent upon each other and cause over regulation. There is no need for automatic regulation of suction pressure in filters, but recording is essential. With regard to undercooling and cake washing it is important to have even throughput. The multi-phase systems under consideration are reversible, indeed, but reversion to homogeneity happens slowly only and requires strong agitation. It never happens on the way from the chillers to the filters even if the feed stock warms up a few C°. It is the reverse process unfortunately which happens within the fraction of a second, because phase separation takes place immediately and throughout the slurry, if temperature is slightly too low. The paraffin crystals then grip tightly the precipitated oil as soon as it separates. This process is hardly visible, but it shows right away in the analytical figures. That is evident from the triangular graphs.



Starting Point A, expressing oil quality, shifts towards the left to B for the separated oil. That means, that if phase separation happened, there is a field of limited miscibility even at properly adjusted temperature, preventing the oil to dissolve unless extended vigorous agitation reestablishes the old equilibrium. It is not permissible to speed up the process by elevated temperature, which naturally would promote homogenization. Its disadvantageous influence upon crystal shape has been discussed in previous articles. It is here where chillers of entirely new design might bring a considerable progress. Slow direct cooling by an evaporating agent, such as dichloromethane, would be a good answer, but the problem is to chill continuously, and it is hard to

~~design a reliable chiller which can fulfil that expectation. Subdivision~~ of the suction pressure into many small steps may come pretty close to the answer, but it is expensive and complicated because it would require a great number of vessels and shock chilling must be avoided under all circumstances. In the ordinary chillers it is to be observed, that the temperature gap between jacket and tube be as small as possible; price consideration of course prohibit to use too many chiller units, and that is why for reasons of heat exchange there will always be a dangerously low temperature in the cooling jacket just at those spots where the menace of phase separation is greatest.

Material and corrosion. There is no need for the use of superior alloy steel or special metals in the construction of a dewaxing plant. The use of light metals or light metal alloys must be strictly avoided, however, if chlorinated hydrocarbons are used as solvents. Especially when dry they can react with light metals vigorously under formation of hydrochloric acid and anhydrous aluminum chloride. The latter one will further react vehemently with the oil, generating considerable heat of reaction and the total effect upon the plant would be disastrous. Some aluminum alloys were tested in hundreds of experiments under various conditions in the laboratory and appeared to be perfectly safe. But the very same alloys reacted just too readily when they were tested in an industrial plant. It is true that this reaction can be inhibited if the solvent is kept wet. Moisture is undesirable in the plant, however. Although dichloroethane and dichloromethane are among the most stable chlorinated hydrocarbons, they still hydrolyze slightly at elevated temperature. This causes formation of traces of hydrochloric acid, which is known to be one of the worst corrosive agents. The oil feed stock is therefore dried, before entering the plant. It is done by submitting it to vacuum at elevated temperature. In spite of all precautions some moisture will always leak into the plants. It accumulates in the wax cake and in the filtrate. Practice proved that it can be kept sufficiently low, if the filtrate is submitted to drying by fractionation in the solvent recovery cycle. It is to be considered that the azeotropic aqueous mixture has the lowest boiling point and is flashed off first.

At this part of the plant it will be advantageous to use a lining with corrosion resisting alloy steel (chromium alloy). It is here where all unfavorable conditions meet, elevated temperature and surplus water. Separation of water and solvent of the condensed azeotropic mixture is done by cold settling. Packing with Raschig rings, gravel or rock salt helps to break emulsions. Corrosions were never found in this part of the drying system, which works at room temperature.

**Pumps** Centrifugal pumps are used for the solvents and wax free liquids. If they are equipped with steam jacket they can also be used for pumping molten waxy products and finished wax. Also gear pumps with steam jacket can be used. Naturally the gears must be protected by screening the liquid before the intake. The pulpy wax cake from the filter is advantageously taken up by a slow motion piston pump with a wide intake pipe and a mushroom shaped intake valve. The stuffing boxes are sealed with graphite rings and metal bellows.

**Filters** The filters are bulky apparatus which are fully enclosed to prevent solvent losses and condensation of moisture from air on the filter cake, or warming up. They must be opened once in a while to replace the filter cloth or to make mechanical adjustments. The ordinary sealing with flange, gasket, bolts and nuts is impractical. Opening and closing is greatly facilitated, if the cover part fits with ample space into a groove, welded around the upper rim of the bottom casing. The groove is equipped with a coil which can be used either for cooling or for heating. When the cover is put in place

~~the groove is filled with a suitable thermoplastic which solidifies after~~ cooling and seals the filter tightly. The cover can be lifted off easily when the heat is turned on in the coil and the sealing agent has melted. Sealing with a two layer combination proved advantageous. The groove is half filled with paraffin which is hardly affected by the solvent but may have cracks for reason of high coefficient of contraction. After its solidification the groove is filled up with a second layer of asphalt which alone is not solvent proof but gives a perfect seal on top of the paraffin. Inorganic salts like sodium sulfate were also tried out and worked satisfactorily. A synthetic plastic which is solvent proof would still be better but has not been tried.

Many devices were tried to insure even distribution of the wash liquid. All sorts of nozzles and sprays were discarded. They are too sensitive to obstruction and traces of paraffin in the wash liquid will occur occasionally in a dewaxing plant. Rotating brushes were very good distributors and gave especially favourable results on drum filters. For band cell filters they were inferior to the simple notched distributing grooves, which are simpler in design and worked satisfactorily.

Connections to the various pipes for solvent, suction or pressure are sealed with metal bellows, leather or solvent resisting synthetic rubber. Leather proved to be best for slides on plane faces.

Level controls. Simple devices serve to indicate the level in the wax cake tanks. The pulpy liquid communicates with a 2 inch wide glass tube outside the tank. A small amount of solvent is continuously fed to the gauge glass, keeping the tube always clean and insuring reliable level indication of the pulpy wax cake. The evaporators are equipped with float type level controls. It is obvious that for paraffinic liquids the float shall not be in a separate casing which is attached to the vessel by tubes. Such arrangements fail always because the tubes get choked by frozen wax. A float inside the main tank with lever, shaft and stuffing box worked satisfactorily and the same holds true for float casings which are directly welded to the tank. Magnetic float impulse transmission to avoid stuffing boxes were considered but could not be tried. For non-waxy liquids any good type of level control will be suitable. The float controlled the valves in the ordinary way by air pressure.

Coolers All paraffinic liquids are led in even flow to the cooling water in the jacket of water cooled scraperless precoolers. Paraffin coating of the walls becomes negligible then, if careful attention is given to temperature control.

Chillers with scraper. Solvent which is likely sometimes to contain paraffin by carry over from low pressure evaporators should be collected separately and used for diluting the charging stock. If such solvent is to serve as wash liquid at low temperature it can be cooled in scraper type chillers only, which increases installation costs unnecessarily. The chillers with scraper are costly and sensitive, but still unavoidable equipment for cooling the oil to dewaxing temperature. They are operated by cold circulating liquid $SO_2$ or ammonia and the considerations of phase rule laws have there to be observed with more care than anywhere else in a dewaxing plant. Perfect temperature control and smallest possible temperature gap are necessary and refrigeration by direct evaporating of refrigerants in the jacket, which was done in plants of older design, will never give satisfying results. Contradictory principles must be compromised with, ~~e.g.~~ that better heat economy by countercurrent involves higher danger of phase separation and even flow of the cooling agent and the oil is therefore much safer although it is inferior economically.

The quantity of oil entering each one of parallel working filters shall be recorded and automatically controlled. It is imperative to have by-passes to each filter which should be instantly operated if irregularities happen. The tube bends have no scraping outfit and may get choked by wax. Even partly choking is harmful because it influences time of stay in the chillers and temperature equilibrium. The bends should not be insulated but rather have a heating coil around the outside. A special design in which a gear driven pending chain cleared the inside of the bend did not work reliably. In recent development the scrapers are extended close to the bends which made wax deposits in the bends negligible and special precautions unnecessary. Dangerous stresses from expansion or contraction are taken up by compensators. The supports of the scraper shaft are designed to stay rigidly in place to avoid damaging of the scraper blades.

Dilution It is advantageous to add the diluting solvent in steps. The separation of crystals from more concentrated solutions happens frequently in form of clusters which hold back more oil in capillary spaces, indeed, but which are more stoutly structured. If such a system is diluted, the oil will distribute evenly by diffusion and the crystals show the favourable slow growth which is specific to crystallization from diluted solutions. The difference is but slight under the microscope and sometimes even not noticeable, but such a treated batch has definitely superior filter rates and gives the same quality paraffin as a check stock which was diluted with the total solvent quantity in one batch and chilled under the same conditions and with observation of all precautions. From the phase rule view point such a procedure is also favourable because the boundary line of phase separation is then remote during the crystallization of the bulk of paraffin, but of course all precaution must be observed just the same for the end of the chilling procedure. It is doubtful whether or not there is an influence upon the equilibrium of oil adsorption to crystal surface. In homogeneous phase it will be only minute and heterogeneous phases, for which it would be of considerable influence must not happen anyway.

Drying of oil. The oil is heated to 120 - 140 C° and pumped to the top of a vertical tank which is fitted with baffle plates in its upper half. Ejectors have been tried for producing the necessary vacuum, but rotating pumps seem to be preferable in spite of higher installation costs. Vacuum shall be a few cm Hg abs. and frothing is readily counteracted by slight increase of temperature, depending upon viscosity of the oil and its moisture content. It is evident that in this case as in all others where liquid may condense on the pressure side of the pump it is essential to have amply designed separating vessels or traps installed.

Tubes in heaters and coolers are rolled and welded into the supporting plates. The floating bundle type is used for apparatus of considerable length. This precaution was taken over from plants which worked with sulfur dioxide as refining or dewaxing agent and was there imperative. It proved to be advantageous for plants with chlorinated solvents also, even though the chances of corrosions are then but trivial.

Safety devices. Pressure vessels are protected by safety valves instead of break plates which were unreliable for the comparatively low pressures which occur in dichloroethane dewaxing plants. They have to be checked once in a while, but never showed corrosion or sticking. The advantages are, that they cause less solvent loss and confusion of operating crew than a ruptured plate which makes them preferable.

Meters for charging stock and finished products are of the oval gear type. Recorders and controlling instruments for all other liquids work on the orifice plate principle. It is important, that the capillary tubes which transmit the impulses to recorders and control instruments must permanently stay free from impurities. They are therefore continuously rinsed by a small steady stream of perfectly wax free oil or solvent. This shall be done for diluted waxy liquids as well as for wax free ones, because there is always danger of wax scales penetrating into the capillary tubes and but little is needed to choke the lines and render the instruments ineffective. A small piston pump, such as is used for feeding oil to pressure bearings, will serve the purpose.

Concentration control of the mixture of the two solvents determines selectivity of the diluting agents which controls the quality of the feeding stock for the filters. Various principles have been tried to insure the production of a homogeneous solvent, but it seems that the apparatus which are based upon measuring of the specific gravity are the most reliable ones. It is to be considered, that the solvents are seldom pure individuals and that they are also sometimes contaminated and colored by traces of oil. The reading of solvent composition is therefore taken from a thermostat controlled side stream on a hydrometer which is enclosed in a casing between plane-parallel glass walls. The hydrometer is advantageously calibrated in % $CH_2Cl_2$ : $C_2H_4Cl_2$. The controlling mechanism is either operated by the hydrostatic pressure of a liquid column or by the buoyancy of a float. No satisfactory results were obtained with a balance arrangement in which the liquid was continuously fed to a large, ball shaped metal container through flexible metal tubes. The weight of the container acted upon levers and a diaphragm arrangement. Controlling instruments based on dielectric constant and electronic amplification came never beyond the laboratory development stage. They were sensitive to impurities and costly.

Jackets The special properties of the charging stock require some precautions. It is evident that all tubes and vessels and the bottoms of evaporators which hold waxy material must be fitted with steam jackets.

The gas, which is used for blowing off the filter cake may be ordinary air. It should be dried, of course, and recycled. Although its heat content is low it must be precooled before entering the filters. The gas holder, which serves to keep the system well balanced shall be sealed towards the atmosphere with gas oil. Its flow rate is suitably measured with Rota-meters, based on the indication of a rotating float in a tapered glass tube.

The decision if the plant shall turn out one or several grades of paraffin depends on what is wanted. There will be a market for a wax which contains the sum of high and low melting paraffin hydrocarbons. The plasticizing and adhesive properties of cyclic waxes blend favourably with the harder straight chain paraffins for all sorts of coatings for atmospheric protection. If special applications are considered, for example, oxidation to fatty acids in which average molecular weight straight chain hydrocarbons are wanted, it is necessary to use suitable cuts and split filtration into steps. The manufacturer of synthetic lubricating oil can use a total wax of any molecular weight and its chief request is that it be oil free. It will also be advantageous to subdivide filtration of heavy ceresinic stocks. The lower melting part blends readily with all sorts of solvents and can be used for the manufacture of many technical products. The high melting constituents have higher market value, because they can replace high priced high melting natural waxes to a certain extent, and a small addition to polishes gives them a glossy finish. They do not blend with solvents very well, though. Some light cuts may not give a wax of commercial value. Filtration in two steps will then produce a commercial wax and a low melting product which can be cracked if it should be unsuitable for other purposes. The microcrystalline structure, chemical inactivity and high melting point of some synthetic paraffins from carbonmonoxide hydrogenation may make it advisable to separate them from lower melting components and to produce waxes which melt above 100°C and are capable to impregnate fabrics or other material to make them waterproof and laundry proof. Preliminary experiments were promising. Naturally, subdivision of the filtration into two steps will increase the installation costs.

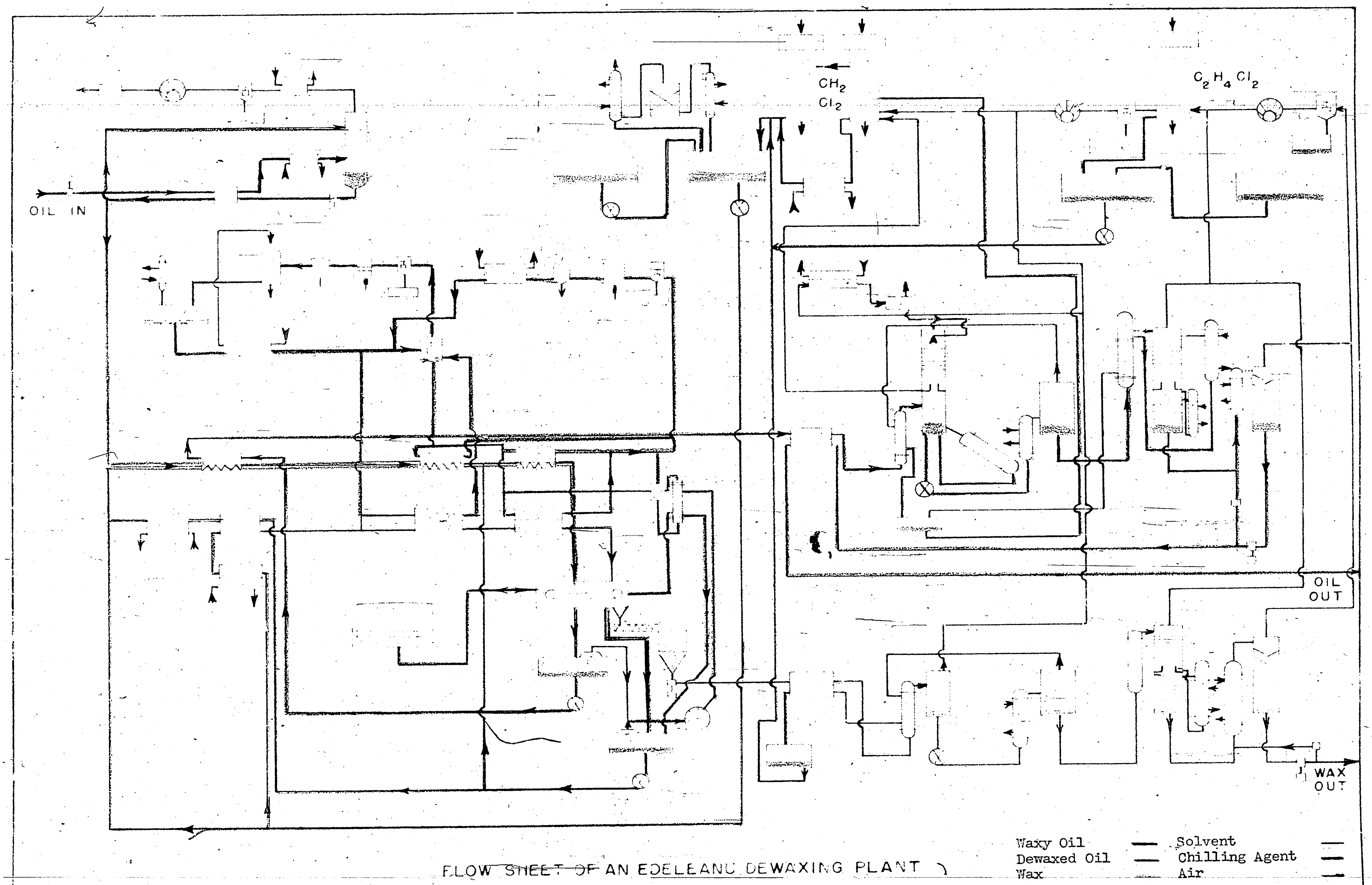
EDELEANU DEWAXING PLANT

The following flow sheet gives the general lay out of a one stage dewaxing plant according to the EDELEANU process. The charging stock enters the plant and is deaerated and dried. It is prediluted with dichloromethane-dichloroethane wash liquid which passes some of the chillers, is further diluted, passes the rest of the chillers and goes to the filters. Filtrate and wash liquid are collected separately. The filter cake drops into a conveyor and enters the solvent recovery and evaporating system. Methylenechloride is flashed off in the first stage which is heated by dichloroethane vapours from the second evaporator. That second unit is steam heated and removes the largest part of the solvent, the rest of which is evaporated in the following stages.

The recovery of solvent from the filtrate is effected much the same way. After having passed the heat exchangers it is freed from the major part of dichloromethane, but precautions are taken that the chemical is dried. In the last stages it is to be observed that temperature be kept below 140 C° to avoid thermic decomposition of the solvent. The evaporators have special design with regard to the moisture control in the plant.

The wash liquid serves to dilute the charging stock.

Liquid traps with automatic check valve protect the rotary gas pumps and compressors. Condensers and heat exchangers are of the shell and tube



FLOW SHEET OF AN EDELEANU DEWAXING PLANT type. Inert gases are bled off. The air bleeder works in two steps, one at room temperature, the other at - 20°C.

Chilling is done indirectly with sulfurdioxide or ammonia. The cooling side is naturally strictly separated from the treating part of the plant.

## Other Dewaxing Ideas

a) Catalytic process It sometimes happens, that light oils and tars which are low in wax content do not bear dewaxing costs. Still there remains the problem to depress the pour point by a cheap process for the production of Diesel fuels, lubricating oils or ordinary fuel oil. Not much attention is usually paid to the wax which is mostly of inferior quality and need not be isolated. It was for these cases, that catalytic destruction of paraffin was studied. Based on the observation that silver catalysts are able to cause catalytic cyclization of heptane to toluene it was tried to break down paraffins to low melting cyclic compounds under mild conditions. The oil in liquid phase was pumped through a coil which was packed with catalyst and arranged in a lead bath. Silver proved to be little effective and after more favourable experiments with alcalis, alcaline earths in form of their oxides and hydroxides it was finally replaced by 1-5% caustic soda or potash on bauxite or siliceous supports. Temperature was maintained at 400 - 420 C° under 30 atm. hydraulic pressure. Pour points could be depressed from + 10 C° to - 20 C° in average. It was found that this depression was partly caused by cracked products, because after redistillation of the oil the pour points climbed to -10 C° or higher. When the still bottoms were blended back again they caused the pour point to drop to its former low. Wax was still present in the oil, but obviously a different crystalline form. The catalysts had no long useful life. After 2 - 3 days they became less effective through carbon deposit, which finally led to obstruction of the coils. The experiments had to be interrupted at an early stage and all data were destroyed. It seems possible however to develop a mild catalytic cracking process for specific destruction of paraffin wax in mineral oils, whereas there is only little chance to adapt it to brown coal tars which are much more unstable and cause quick contamination of the catalyst by deposit of carbon and polymerics.

b) Dewaxing by mechanical vibrations. It is known that mono- or polyvectorial vibrations are capable of shaping powders into hard solid plates. It therefore seemed possible to deoil wax scales by such a process. A wax cake with 40% oil content was submitted to vibrations of 100 cycles per second with 1 mm amplitude. The cake in its container got a smooth surface but no indications of oil separation from wax could be observed after half an hour treatment. Analysis of the wax cake after the test showed even composition throughout. Variation of frequency and amplitude or superposition of vibrations did not give better results either. Supersonic waves will be more powerful, but no suitable generator was available for experiments. It can be expected, that oil is squeezed out from wax cakes between the nodal points, but it remains doubtful if the effect is satisfactory and it will certainly not be quantitative. The procedure can be compared with pressing, of a cake, which is subdivided into thin layers, spaced by the wave lengths.

c) Dewaxing with surface active agents. A waxy oil represents a system of balanced molecular forces. These forces can be measured and are chiefly the cohesion of the oil, expressed by its surface tension $\alpha$ and its adhesion to paraffin $\beta$ which can be measured by the depression which a capillary column of oil suffers by the pull which is exerted by oil wetted paraffin. Surface tension is readily measured by ascension in capillary tubes and calculated from

$$\alpha = C \cdot \delta \cdot \frac{h}{10} \quad \text{dyn/cm}$$

in which $\delta$ means specific gravity, h rise in capillary tube and C capillary constant. The adhesion is measured by counteracting the capillary ascension with a narrow slit of the material to be tested and into which the capillary tube is immersed. The slit pulls the oil back to a new height $h_1$ and $\beta$ can be calculated from:

$$\beta = \delta \cdot \sigma \cdot 49{,}05 \, \frac{h - h_1}{10} \quad \text{dyn/cm}$$

in which $\sigma$ stands for the width of the slit. $\alpha$ and $\beta$ depend on temperature as it is known and can be contracted to an expression which is independent from temperature $\frac{\beta}{\alpha} = \cos \varphi$. For the dewaxing problem it is more advantageous to consider both separately, however. The surface tension can be easily influenced by additions. It is the force which pulls the liquid back into the liquid phase and the higher it is, the less readily is the oil bound by forces of adhesion to the solid boundary. On the other side will a lowered surface tension help a liquid to spread over boundary surfaces. A liquid, which has very low surface tension and is immiscible with oil will therefore push it away from crystal surfaces and replace it.

The adhesive force $\beta$ results from the various attracting momentums of the solid. It is usually beyond external control.

The adhesive force of oil to wax is very large and no additions of chemicals to oil could be found or are likely to be found which increase surface tension of the oil sufficiently to overcome the attractive forces of adhesion. The only feasible way was therfore offering the wax another liquid with low surface tension. Of course, the dilution with solvents may act this way, but we want to consider heterogeneous systems, Such a liquid is water with the addition of surface active agents such as laurylsulfonate, A wax cake with 38% paraffin content and 40°C melting point was vigorously shaken at room temperature with twice its volume of a 1% solution of laurylsulfonate in water. The waxy layer was separated and now contained 72% of paraffin with 49 C° melting point. Also more encouraging results were obtained, but the data are no more available. One drawback of this method to wash the oil simply off the wax crystals is the difficulty to break the emulsion of oil in water, and to recover the active agent. Even the best results were far inferior to any commercial dewaxing process but the method still has future prospects, It works on a principle which is entirely different from the known processes, eliminates the dilution with solvents with all their drawbacks or reduces it considerably,

d) Dewaxing by diffusion. The elimination of filter cloth and costly rotating equipment would mean a remarkable advance even if solvents were still needed. It was tried to accomplish dewaxing by diffusion under observation of phase rule considerations discussed above. Preliminary tests with separating diaphragms gave encouraging results even with non selective solvents such as benzene and some chlorinated hydrocarbons. But diffusion was too slow, amount of solvent needed too high, and separation of wax from oil unsatisfactory. The diaphragms were then eliminated and oil and solvent ~~was~~ contacted in horizontal tubes. Heavy solvent filled the tube half way and the thin waxy oil layer was floating on its surface countercurrently. The results were not satisfactory. Finally the waxy oil was sprayed by a nozzle against a large, cooled rotating drum on which it solidified in a very thin layer. The drum immersed in cold solvent and most of the oil was dissolved, leaving fairly clean wax on the drum, from which it was continuously scraped off. Although this apparatus worked fairly well it still did not answer the demand for a completely oilfree wax and the chief drawback was, that wax scales were washed off the drum, contaminating the liquid and causing bad pour points.

Dewaxing with electricity. No results were obtained in exposing thin or thick layers of wax cake to the influence of a few thousand volts D.C. which may be attributed to the unsatisfactory and improvised experimental equipment.

A few experiments were done to sweat filter cakes by the influence of high frequency currents. The idea was that polar and viscous compounds get heated under those conditions while the waxy component was supposed to stay cold and solid. The oily wax was exposed to the electric treatment between condenser plates in an inductively coupled circuit. A sweating effect could be observed but no data could be evaluated because the equipment was destroyed. Such a process would probably have a very limited economic field only, but may permit new conclusions because it means selective application of heat to waxy systems.

Supersonic waves. No improvement of a dewaxing stock could be observed if it was exposed to vibrations during chilling. The idea, that considerable compressing forces which are spaced by the wave length might congregate the plastic crystals to small oilfree globules which have most favourable filtering properties could not be confirmed. Naturally there remains the possibility, that more powerful apparatus and especially supersonic waves give different results, but it is doubtful if such a process could work economically, considering the large throughputs in dewaxing units.

Filter aid It was tried to use frozen water globules as a filter aid. A mixture of water and solvent was chilled under vigorous agitation. The slurry, added to the dewaxing stock gave only slight improvement of filter rates. This and the danger of hydrolysis of the solvent in recovery, caused me to stop further work in this line.

Magnetic dewaxing It was tried to crystallize the wax around iron nuclei. Iron reduced from oxide and from carbonyl was tried. Some wax could be separated in a strong magnetic field, but it was never possible to separate all the wax and neither could it be obtained oilfree. There seems to be a tendency of the wax crystals to reject the metallic iron rather then to surround it and the experiments were abandoned.

Dewaxing by solvent extraction. Solubility of paraffins, especially of straight chain waxes in selective solvents increases less with growing temperature than that of other mineral oil constituents. This fact becomes particularly evident with highly selective solvents such as acetone or sulfurdioxide. It was tried to remove the oil from waxy distillates or from oily slop wax by extraction with liquid sulfurdioxide at temperature above 100 C°. Neither batch extractions nor countercurrent treatment with temperature gradient gave satisfactory results. With commercially bearable solvent quantities the raffinate layer always still contained in average 20% oil in the paraffin. The extracted oil on the other side held very much wax. This wax could not be isolated because phase separation happens in chilling resulting in an oily wax layer and the usual extract. From the phase rule view point there is little chance to get better results with any solvent. The isolation of a small amount of pure wax will be possible with much solvent but a complete economic separation of wax and oil is beyond any possibility.

Miscellaneous

1) Moisture or Humidity Recorder

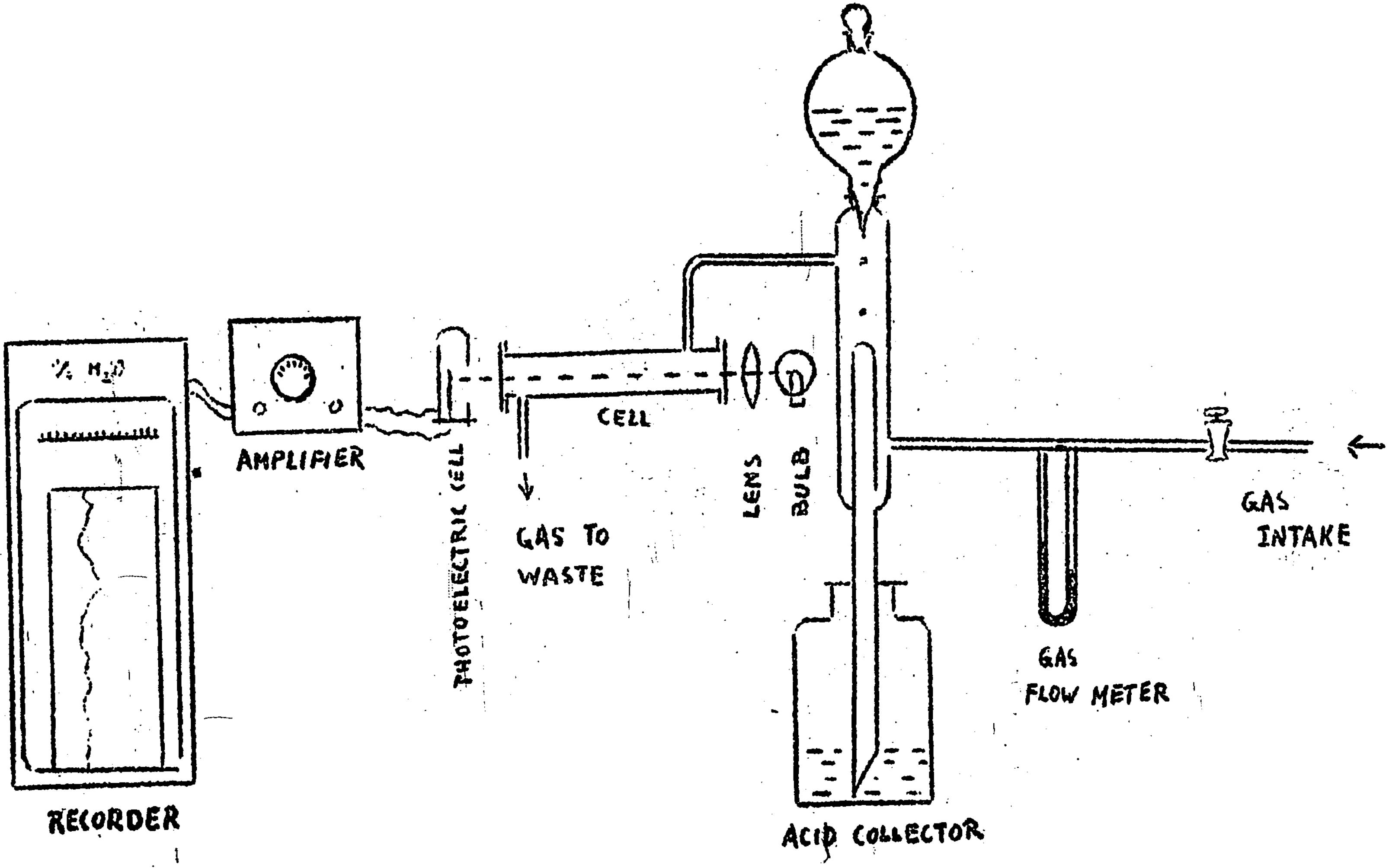
The refrigerating unit of some solvent refining and dewaxing plants which operate on liquid sulfur dioxide is closely coupled with the treating part of the plants. This makes it imperative to watch closely the moisture content of the liquid sulfur dioxide in order to avoid corrosions. ~~Various~~ methods have been suggested for that particular task but proved to be unreliable in practice. The difficulty lies in the fact that the water content of the $SO_2$ is minute in any case. A higher moisture content than 0.1% per vol is already objectionable. It is demanded to record water content between 0.001 to 0.100%. The liquefied gas is usually contaminated with more or less heavy oil in a percentage as high as 1%. Purely physical methods failed under those conditions, because the influence of the impurities is prevalent and covers the change of physical properties by traces of water. No success was obtained in measuring surface tension, refraction, conductivity, density, dielectric constant and other data. Of the chemical methods the titration with iodine-$SO_2$-pyridine solution which I published in 1935 proved to be serviceable. It was tried to develop a recording instrument on this principle. Measured quantities of liquid $SO_2$ and of iodine solution were continuously fed to a glass chamber, through which a beam of light was transmitted. A photoelectric cell and amplifier gave alarm when the moisture transgressed a given limit. Continuous recording of the moisture content by this method was costly and difficult, however, and the device was abandoned. I therefore decided to choose a much simpler and cheaper principle which, worked very satisfactorily and shall be described, because it is also practicable to control the moisture content of many other gases besides $SO_2$ and may be of interest to some producers and gas bottling firms.

It is the gas phase which is examined for moisture and which, at a given temperature, also depends on the water content of the liquid phase. In most cases it is the humidity of the gas phase only that matters anyway.

A small, unmeasured gas current is contacted with a small unmeasured surplus of fuming sulfuric acid. This acid releases continuously some anydrous gaseous sulfurtrioxide which hydrates readily to a very stable mist of sulfuric acid when in contact with a gas which holds traces of moisture. It was found that the optical density of that mist is in simple relation to the humidity, if it is low and preferably just within the desired limits of 0.100 to 0.001%. It is evident, that any gas or vapour, which reacts chemically with sulfurtrioxide or fuming sulfuric acid cannot be examined for water with this method, but it is very suitable for all sorts of non reacting gases such as sulfur dioxide, nitrogen, oxygen, carbon dioxide and others. Impure sulfur dioxide which contained oil could also be accurately analyzed by evaporating the liquefied gas at low temperature, (-10°C) where the gas was free from impurities, while it still held water in measurable quantity which could be readily recorded.

The recording apparatus was as follows:

A gas stream of 20 - 100 cc per minute is roughly measured by an orifice meter and enters the saturator. This is a glass vessel in the shape of a vertically mounted cooler jacket. The inside of the jacket is fitted with a distributor which spreads the small amount of fuming acid over a larger surface and gives the passing gas a chance to pick up sulfurtrioxide. The fuming acid is admitted to the top of the distributor dropwise at a rate of one drop every 10 - 20 seconds. Spent acid is continuously drawn off by collecting flask and syphon arrangement. The spent acid must still be fuming. It shall be avoided to contact the gas with very large quantities of acid or to bubble


% H2O
RECORDER
AMPLIFIER
PHOTOELECTRIC CELL
GAS TO WASTE
CELL
LENS
BULB
ACID COLLECTOR
GAS FLOW METER
GAS INTAKE

~~it through acid which then acts as a desiccant.~~

The gas - acid mist enters a cylindrical glass chamber 15 cm long and 4 cm wide with plane parallel cover glasses. They shall be sealed to the chamber with an acid resisting adhesive, which permits to take them off for cleaning in intervals of a few weeks. The light was supplied by a 6 V, 5 Amp. bulb focused by a condenser lens couple. Some mist will deposit on the walls and give a small amount of acid which shall be removed from time to time. (Once a week).

The light beam, after having passed the chamber hits upon a photoelectric cell. Amplifier and milliampere recorder complete the equipment, For a given gas and given conditions the milliampere recorder can be calibrated in % moisture. The deflection was almost logarithmic and readings to fractions of 1/100-percent moisture could be made with sufficient accuracy. The readings were frequently checked by titration and proved to be reliable. The apparatus is simple in design and easy to clean when necessary. It can be further simplified by using a photovoltaic cell, and depressor bar recorder or alarm instrument.

2) Level indicator and control

In solvent refining and dewaxing with benzene-$SO_2$ mixtures, sometimes considerable difficulty was encountered in finding the separation line of 2 liquid phases. This was particularly the case in high temperature extraction of heavy lub oils with benzene-$SO_2$ when the black color made gauge glasses useless and the high pressure caused us to abandon floats and unnecessary stuffing boxes. The new apparatus which was designed for those special cases was based on the difference in dielectric constant of $SO_2$ and oil or benzene.

The principle of the arrangement was superposition of two tuned radio circuits and recording the beats of interference.

One high frequency circuit had a fixed wave length. It consisted of the simple well known arrangement of tube, condensor and coils. The second circuit was similarly built but its condensor was partly formed by two metal strips within the critical zone of the treating tower, introduced through its walls by spark plugs. Its capacity was therefore variable and depended upon the dielectric constant of the liquid and also upon the location of the separating line between the two liquid phases. Superposition of the 2 vibrations in a third circuit gave low frequency beats which were transmitted to a vibrating reed frequency meter. That meter read directly level height within the tower.

The device was later abandoned because it was too sensitive and the indication of the frequency meter gave correct readings for fixed operating conditions only and varied greatly for various oils, different solvent composition or other treating temperature. It is only mentioned because it may be useful for a special problem.

3) Another much simpler level indicator was designed and widely used in plants afterwards. I later learned that the principle had also been independently developed in Holland. It was based on dielectric constant, alternating current and the use of condensers. It was believed that A. C. was not flowing in sufficient strength in a circuit, consisting of a small condenser, neon lamp and A. C. source, if the condenser plates were immersed in oil with low dielectric constant, but that the neon lamp should light if a medium of high dielectric constant gave the condenser a higher capacitance. The effect was actually observed for oil -$SO_2$ and similar systems and in extraction and dewaxing plants working with sulfurdioxide (which has very high dielectric constant) that indicator was used with advantage. The voltage was 110 - 220 A. C. Spark plugs with electrode plates installed in different height of the

vessels served as condensers. The circuit was protected by high ohm resistors and lighting of a neon lamp indicated with certainty the height of the liquid level. It was soon found however that the theoretical presumptions were wrong and that lighting of the neon lamp simply depended on ordinary conductivity. The arrangement also worked with D. C. of proper voltage, though not quite so dependably. While oil with 15% of $SO_2$ still left the neon lamps dark, $SO_2$ with as much as 40 - 50% oily extract components was sufficiently conducting to light the lamps brightly. Numerous experiments had shown that a spark of 2 - 3 milliamps under 110 - 220 volts could not ignite gasoline-, ether-air mixtures, but safety regulations demanded the enclosure of all current leading parts in explosion proof shells.

4) Alarm device for indication of excessive water

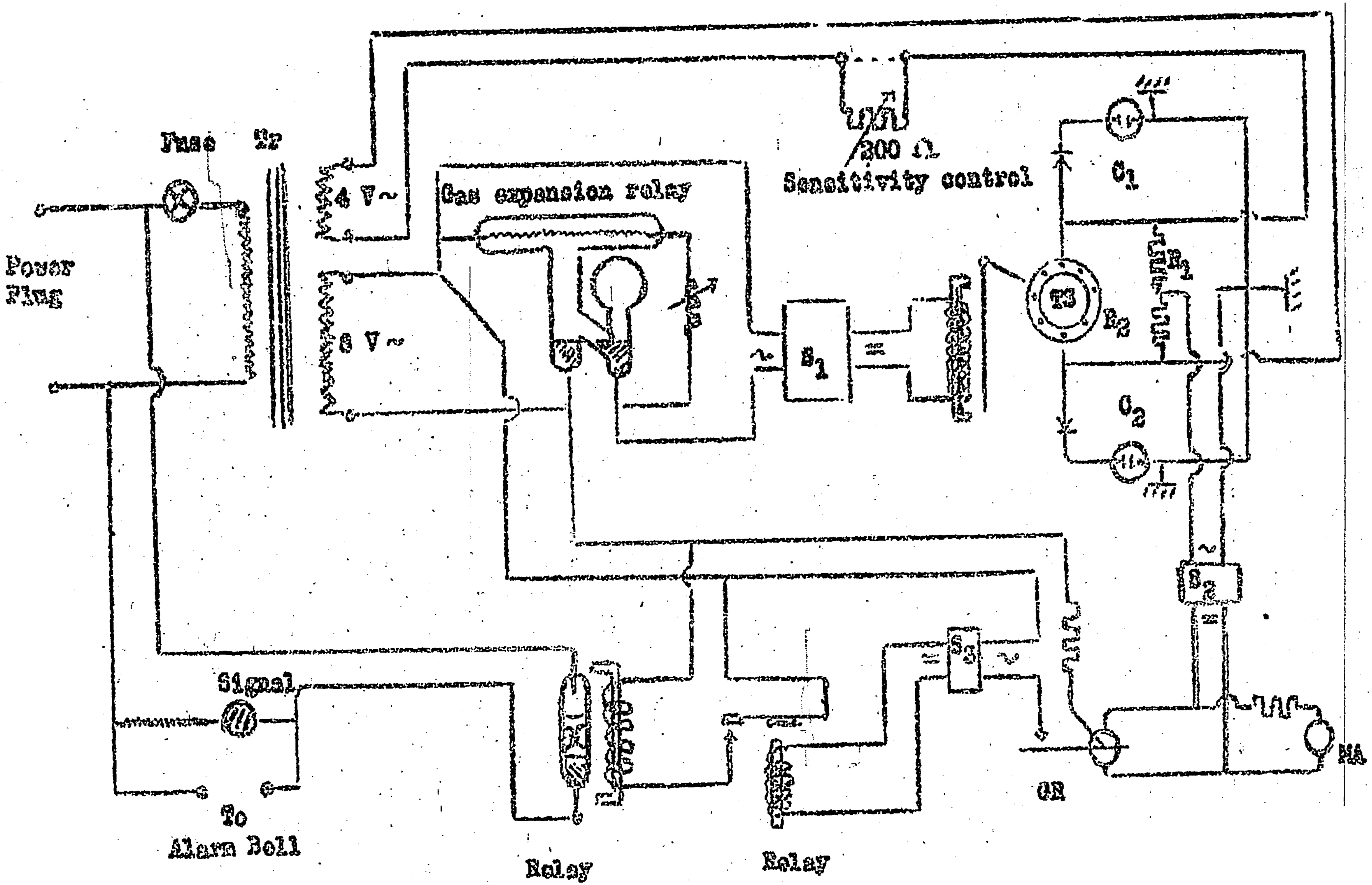
It is disadvantageous for any solvent refining or dewaxing plant if water is carried into the plant with the oil. Flooding with water would be disastrous for plants which work with $SO_2$. Water interferes with the operation considerably in any plant which works with solvents for reason of hydrolysis (chlorinated compounds, esters), contamination of filter cake or change of selective properties. (Phenol, acetone etc.)

A simple alarm device tells with certainty if the hot feed stock carries water. It consists of a cone shaped vessel, holding 2 gallons, which is installed in the pipe which feeds the plant with light cuts or hot lub. oil distillate. Two spark plugs are screwed into the lower tapered part of the vessel, approximately 2 inches from the lowest part. The vessel is filled in its lower quarter with rock salt. Oil inlet and outlet are opposite on the top part. The spark plugs are permanently connected with a battery and a bell. While traces of water in dry oil do not have any effect, the bell will give alarm immediately when the salt is dissolved by a batch of water.

5) Corrosin indicator.

An apparatus of simple design was developed to indicate corrosion and leaks in solvent refining and dewaxing plants. (Especially for $SO_2$ as solvent). It measured the conductivity of cooling water before and after the heat exchangers and of water from steam traps against a fixed resistor. The Wheatstone bridge principle was used. A gas expansion relay advanced the contact brushes of a telephone line selector intermittently and with adjustable speed. It thereby connected successively up to 12 couplesof measuring cells with the Wheatstone bridge. The 0- Galvanometer relay operated a relay arrangement and gave alarm if the bridge was out of balance. The conductivity cells consisted simply of T - tubes through which the water passed continuously while its conductivity was measured by an ordinary spark plug to which perforated, concentric and cylindric silver electrodes had been soldered. Conductivity depends on temperature and the T-tubes therefore could be water cooled, but it was found that 25 C° temperature difference of fresh and used water were permissible and did not unbalance the bridge. Small leaks in heat exchangers or evaporators were immediately indicated by the alarm bell. The location of the leak was quickly found from the indication of a pointer, which was fastened to the rotating arm of the line selector and gave the number of the contact couple. The size of the leak could be estimated from the indication of the milliammeter.

No experience was collected with the instrument in dewaxing plants which worked with chlorinated hydrocarbons. Timing of the progression of contact arms by gas expansion relays proved to be very reliable and the performance of the telephone line selector in giving very good contact to many successive contact couples in continuous operation over a long time period was excellent,



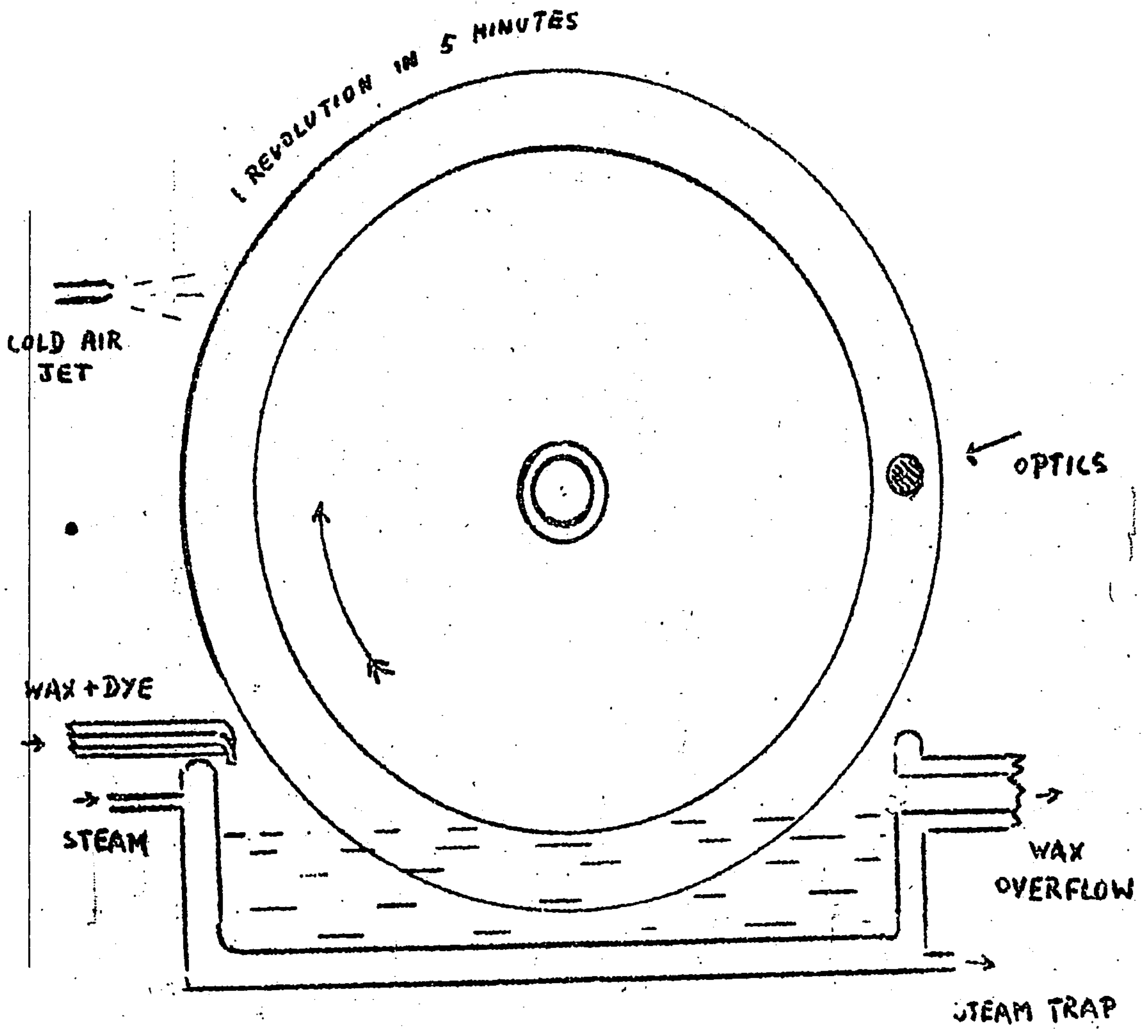
$C_1$ and $C_2$ = Conductivity cells for fresh and used water
$R_1$ & $R_2$ = Bridge resistors 100 Ω.
$S_1$ $S_2$ $S_3$ = Selenium rectifiers
GR and MA = Galvanometer relay and milliammeter
Tr and TS = Transformer and Line selector

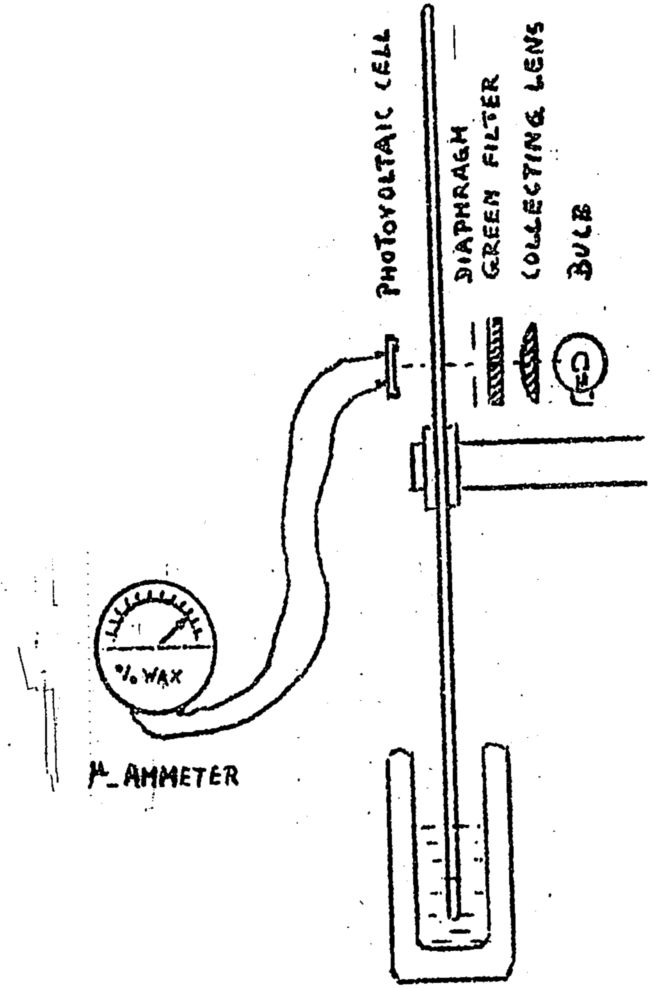
## 6) Paraffin % recorder.

Much experimental work was done to design an instrument which is capable of recording continuously the paraffin content of the solvent ~~free wax~~, before it leaves the dewaxing plant. The principle of transmission of polarized light, which is described in detail in the following article, can only serve for individual analytical determinations. It was tried to dip a large rotating glass disc with its lower parts in a current of molten wax. The wax then solidifies and the homogeneous layer of even thickness can then be examined between crossed nicols. That method failed completely, however, because on uncovered glass surfaces the wax always crystallized in directed crystals and the presumption for the electro-optical analysis is irregular arrangement of the crystals in space.

It seems however, that another way can work satisfactorily, which is based on the dyestuff method (article III).

Some wax from the evaporators is evenly fed to a small vat. On its way it passes adjusting valve, flow meter for very small throughput, and tube with mixing baffles or orifices. Before that mixer a minute quantity of Sudan Red solution in molten paraffin is evenly fed with a diesel oil injector or similar pumping device. Some of the colored solution in the vat adheres to a slowly rotating glass disc. It there solidifies after a few minutes and the color equilibrium is established. The coating on the glass disc remains brightly red colored if the wax contains oil. Traces of oil will result in a slight pink color, and oil free wax shows evenly and faintly grey. That color is measured by an arrangement of light source, diaphragm, photoelectric or - voltaic cell and amplifier with indicating or recording instrument. It is evident, that all wax holding vessels and tubes, except the glass disc, must be steam jacketed. Smooth and even oper~~ation is~~ the presumption for reliable


1 REVOLUTION IN 5 MINUTES
COLD AIR JET
OPTICS
WAX + DYE
STEAM
WAX OVERFLOW
STEAM TRAP


PHOTOVOLTAIC CELL
DIAPHRAGM
GREEN FILTER
COLLECTING LENS
BULB
% WAX
μ_AMMETER

indication. The calibration for wax % is based upon analyses. The small quantity of colored wax is not lost and can easily be refined with sulfuric acid and freed from the dyestuff. A laboratory model could not be brought to perfection but results were encouraging.

This shall conclude the discussion of view points which are important for solvent dewaxing. It is beyond the scope of these pages to deal with the subject more in detail. Of course much remains to be said, and more experimental work shall and will be done. In solvent dewaxing research will find mechanical simplifications of equipment and possibly solvents with superior characteristics.

Dewaxing on other principles than the mechanical separation of the wax by centrifuges and filters is a new field, which has just been scratched by the plough of research. Its possibilities can therefore not yet be properly estimated.

A new analytical method for paraffinic products was developed. The subject does not directly pertain to dewaxing and shall therefore be discussed separately in the following article VII.