This solution contains 2.5 mg. of trichloroethylene per ml.

3. Pipet 1.00, 2.00, 3.00, 4.00, and 5.00 ml. of solution F, 2 into a series of 100-ml. volumetric flasks. Dilute each to volume with xylene and mix thoroughly. These standard solutions contain 0.025, 0.050, 0.075, 0.100, and 0.125 mg. of trichloroethylene per ml. respectively.

General Remarks

The addition of a defoamer to the distillation mixture has been found necessary because certain of the oils, especially crude soybean oils, foam excessively during the distillation. Silicone Antifoamer "A" proved to be the best of the defoamers tested for this purpose.

Some filter papers have been found to bleach the orange colored pyridine solution to a yellow. This is thought to be due to the presence of free acid in the paper. A number of lots of Whatman No. 41 filter paper have been tested to date, and all have been found to be quite satisfactory.

While this method has been written for the use of a Coleman Model 6B spectrophotometer, it is thought likely that any colorimeter might be used satisfactorily. A modified form of this method, employing a Cenco-Sheard-Sanford photelometer, has been in operation for more than a year now.

It is thought probable that this method could be modified to cover the determination of TCE in many other materials beside oil, such as meals, tissues, air, etc.

Summary

An accurate method for determining small amounts of trichloroethylene in vegetable oils has been presented. The method employs a distillation procedure to separate the trichloroethylene from the oil and a colorimetric procedure based on the Fujiwara reaction to determine the trichloroethylene in the distillate. The method has been tested on known samples of crude and refined soybean and cottonseed oils varying in trichloroethylene content from 0.001% to 0.6% with excellent results.

REFERENCES

1. Arnold, Hollowell, Proc. Iowa Acad. Sci., *54*, 181-183 (1947); Sweeney, Arnold, Hollowell, Iowa State Coll. Eng. Exp. Sta., Bull. No. 165, 89 pp. (1949).
2. Barret, J. Ind. Hyg. Toxicol., *18*, 341 (1936).
3. Brain, Helliwell, Biochem. J., *45*, 75 (1945).
4. Bruening, Schnetka, Arch. Gewerbepath. Gewerbehyg., *4*, 740 (1933).
5. Chlorine Products Bulletin No. S 18-949, E. I. duPont de Nemours and Company.
6. Cole, J. Biol. Chem., *71*, 173 (1926).
7. Fujiwara, Sitzber, Abhandl. Naturforsch. Ges. Rostock, *6*, 1 (1914); Chem. Abstracts, *11*, 3201 (1917).
8. Kelly, O'Connor, Reilly, Analyst, *66*, 489-490 (1941).
9. Malisoff, Ind. Eng. Chem., Anal. Ed., *7*, 428 (1935).
10. Rauscher, Ind. Eng. Chem., Anal. Ed., *9*, 296-299 (1937).
11. Schmalfuss, Werner, Z. Anal. Chem., *97*, 314-317 (1934).

[Received January 2, 1951]

Solvent Extraction for the Oil Mill Superintendent[1]

KEATOR McCUBBIN, Chemical Plants Division, Blaw-Knox Construction Company, Pittsburgh, Pa.

BEING directly in charge of operations, the oil mill superintendent is usually held accountable for operating results. Success or failure is easily, and continuously, measurable; since he is held responsible, the esteem with which the superintendent is held by his management is a reflection of his mill's record. Accordingly, in operating a process, or in selecting one for future operation, decisions are usually made by taking the course believed to provide the most favorable answer to the question "How will it affect my results?" Theoretical aspects are given consideration only when they would appear to have immediate bearing on this question.

The success of a solvent extraction mill superintendent may be measured by the degrees to which he attains the following goals:

1. Maintain continuous seven-day operation at full capacity.
2. Manufacture and ship finished products of uniform quality, a quality which is at least acceptable, and preferably superior to that of competing products.
3. Obtain optimum yields of oil and meal.
4. Operate with minimum solvent loss and utility requirements.
5. Operate safely.

It will be seen that these goals are not at all peculiar to the superintendent of an oil mill. If, instead of the words oil and meal, we use the term finished products; and if, instead of solvent loss and utility requirements, we use the term operating costs or direct costs, then these same five goals could be, and are, used by the superintendent of almost any process plant. In the same way the general methods for reaching these goals are similar in all cases.

This paper will be confined to an extraction plant of the standard type. The seed enters the process, is prepared by cracking, adjustment of temperature, and moisture content, and is flaked. Oil may or may not be removed by prepressing. After preparation the flakes are extracted, and the solvent removed from the extracted oil and the spent flakes.

The oil mill superintendent is then concerned with the five goals as they apply to this process.

1. *Maintaining continuous seven-day operation.* In particular, the procedure for maintaining continuous seven-day operation is similar for any type of plant. The superintendent who does not yet have a plant should be given the opportunity by his management to examine the available processes very critically. Common sense and general operating experience will enable the superintendent to determine the points of greatest stress. He should insist that bearing loads are acceptable, that conveyors are adequately designed, and that the equipment selected is rugged and well constructed. The superintendent who is now operating a plant can do much to reduce down time and achieve 24-hour, seven-day operation by systematic study of the causes of breakdowns. It often will be found that a comparatively few weak points in the plant are responsible for a large percentage of the down time.

[1] Presented at the fall meeting, American Oil Chemists' Society, San Francisco, Calif., Sept. 26-28, 1950.

In connection with reduction of down time there is one particular point which should be stressed. It has been found that a carefully worked out lubrication system, one employing the maximum amount of automatic lubrication and a minimum amount of manual lubrication, has been a tremendous aid in reducing wear and breakdown of equipment. If such a system is incorporated in the plant at the time it is designed and constructed, the increased cost is not excessive and can frequently be justified by reduction in man-hours required for lubrication.

2. *Manufacture and ship finished products of uniform quality, a quality which is at least acceptable, and preferably superior to that of competing products.* To produce finished products—oil and meal—of uniform and, if possible, superior quality requires some consideration of the physical characteristics of the oil and meal being produced. Most vegetable oil is sensitive to heat and to air, particularly to air when at elevated temperatures. This necessitates that the distillation system for removing the solvent from the oil be designed to expose the oil to moderate temperatures and to minimize contact with air. As time of exposure is also a factor, the system should be designed for low residence time. Systems are now available which perform the distillation in less than 10 minutes, and at temperatures of 200°F., or below. These systems also have been designed to permit a minimum of air leakage. Older systems operating at higher temperatures and having longer retention time frequently can be improved by proper instrumentation or by the addition of supplementary equipment, such as better vacuum systems. In all cases the superintendent should pay particular attention to distillation temperature, residence time in equipment, and to the prevention of air leakage. Unnecessary holding volume should be located and eliminated.

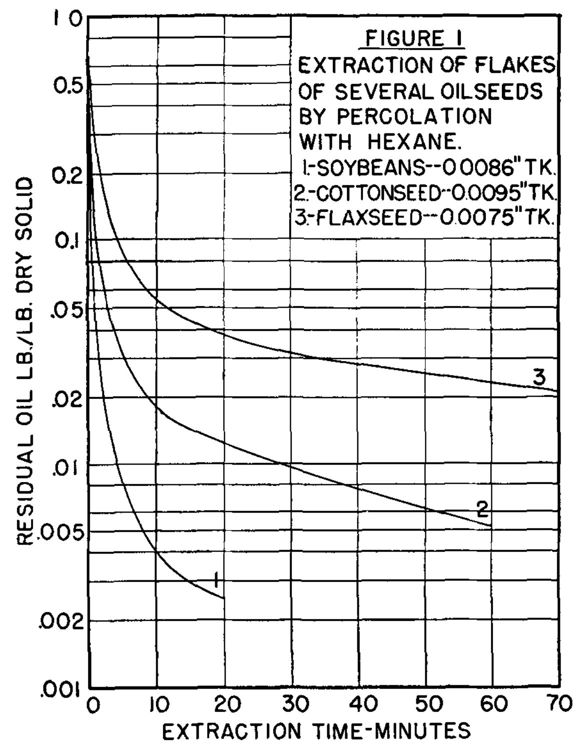
In many older plants a substantial improvement in oil quality could be effected by installing equipment for filtering and cooling the oil immediately after it leaves the distillation system. The oil from these older plants frequently is discharged from the stripping column containing small amounts of undissolved solids and moisture. Removal of the solids and reduction of temperature prior to storage is desirable in this case.

In the case of meal, uniformity and high quality are not easily judged because absolute standards are only beignning to be developed. The criteria for what constitutes good meal have changed somewhat during the past few years; as more objective tests are developed, it is probable that trade demands will modify still more. It is essential that any flake processing system selected today have controlled flexibility to meet changing market conditions. It should be designed for control of time, temperature, and moisture, independent of throughput and of each other.

For the superintendent desiring to improve the operation of the older flake processing system, there is little encouragement. The only really satisfactory way found so far is by the addition of new equipment.

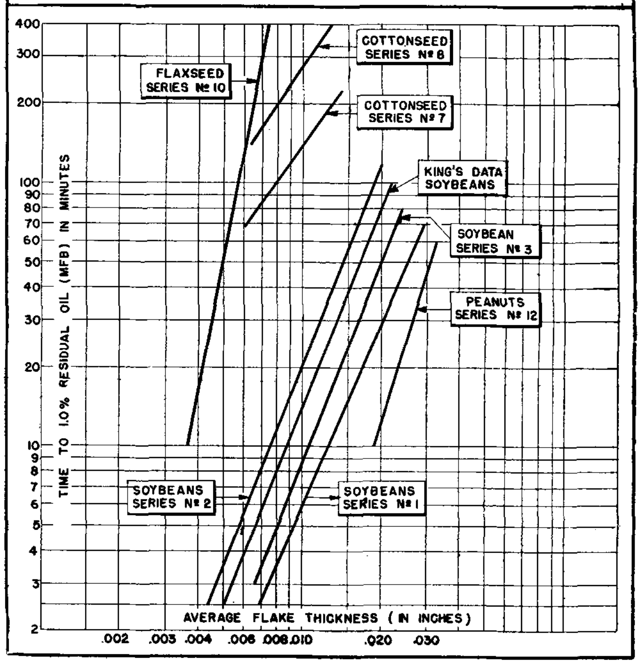
Before leaving the subject of uniform meal, it should be pointed out that the grinding system is a very important factor. Formerly grinding was not considered part of the solvent extraction process but was looked on as an entirely separate operation. As a result uniform, well toasted flakes were often converted to low grade meal by improper grinding. For really good results the grinding system must be selected to suit the characteristics of the material being ground and the desired granulation of the finished product.

3. *Obtaining optimum yields of oil and meal.* Obtaining optimum yields of oil and meal requires proper preparation of the seed and proper extraction. With any given equipment the plant superintendent may control, within limits, the size of crack, flake thickness, the bulk density of the flake, and the extraction temperature, extraction time, and the solvent ratio, or pounds of solvent per pound of flakes extracted. To control these variables properly it is not necessary to have a complete knowledge of the complicated mechanism by which oil is extracted from seeds. It is necessary however to have a proper grasp of a few elementary facts. Some of the more important are demonstrated by the following illustrations.



In Figure 1 flakes from different oil seeds vary considerably in extraction rate even with identical preparation and the production of flakes with the same thickness. It is obvious from this illustration that a plant designed for and attaining a given throughput on one seed will not necessarily give the results when operated with the same throughput on another seed. This illustration also shows that most of the oil is easily and quickly removed while the last portion is removed very slowly. It has also been proven that the more slowly extracted fraction contains a higher percentage of foots. It is a combination of the decrease in extraction rate and the increased content of foots in the extracted oil which fixes the minimum acceptable residual oil content for any given seed. Finally this illustration shows that some of the oil probably cannot be extracted at all. The curves all tend to flatten out, indicating that beyond a certain point no amount of extraction would improve the

FIGURE № 2 - FLAKES
EFFECT OF FLAKE THICKNESS ON EXTRACTION TIME



results. Regrinding is necessary for complete oil removal.

Figure 2 indicates the effect of flake thickness. Examination of this illustration indicates clearly that one of the easier ways to improve extraction for any given extraction time is to reduce flake thickness. This illustration also shows the importance of using flaking mills which can be controlled within close limits.

Other factors being equal, best oil recovery will be obtained by the mill producing the highest percentage of thin flakes, provided these flakes have sufficient uniformity and mechanical strength to withstand breakage and disintegration during extraction.

Figure 3 shows the relationship between extraction rate and temperature. As would be anticipated, increasing temperature decreases the extraction time necessary to reach a given residual oil content.

Usually it is easier to increase the extraction temperature than to change any other variable. If the solvent heating capacity is limited, an additional heater can be installed cheaply.

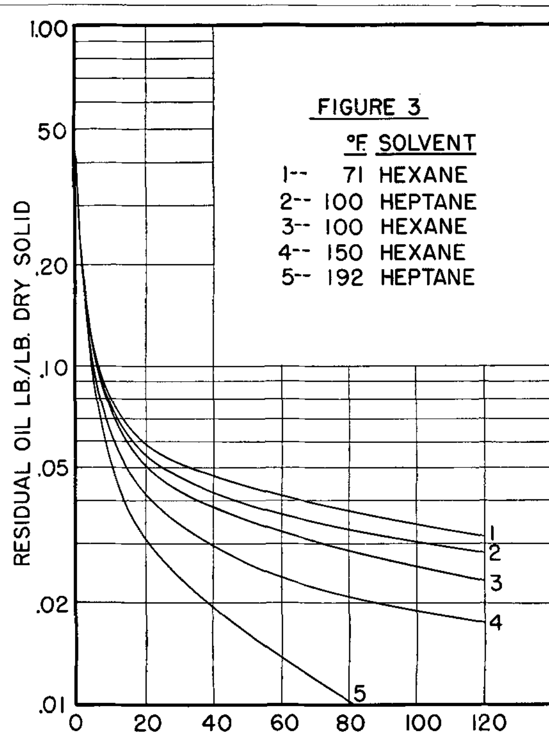
Incidentally, it should be pointed out that temperature and flake thickness ordinarily have more effect than solvent ratio on results. If the solvent heating capacity is limited, increasing the solvent ratio may lower the extraction temperature and actually impair the efficiency of extraction. In these cases it may be possible to improve results by decreasing the solvent ratio.

4. *Operating with minimum solvent loss and utility requirements.* Minimizing solvent loss and utility requirements is really a whole series of operating problems. The superintendent's standard for solvent loss, steam consumption, and water usage usually is the manufacturer's guarantees. Manufacturer's guarantees are too conservative to be good standards; they invariably contain a margin of safety. Any well run plant should stay well below the supplier's guarantees for solvent loss, steam, water, and power usage.

Solvent loss other than such leaks as are permitted to occur at stuffing boxes and similar places result from absorption by the meal and dispersal in air which enters the system. Preventing loss due to leakage is fairly obvious and in most plants is given careful attention. The only point meriting mention with regard to leaks is that solvent, unlike oil, is volatile. Leaks are not always readily apparent. A periodic pressure test for all piping and vessels normally containing solvent may locate many unsuspected leaks.

When consideration is given the fact that a pound of air at 80°F. may carry one and one-half pounds of hexane, the importance of loss due to air is readily understood. Formerly attempts were mainly along the line of reducing the concentration of solvent in the air by refrigeration, carbon absorption, or scrubbing. More recent progress has been made by reducing the amount of air permitted to enter. In several cases it has been possible to design so as to reduce air flow to such a point that satisfactory low solvent loss is obtained by the use of a water cooled vent condenser not followed by refrigeration, carbon absorption, or scrubbing. In one particular case the flow of vent gases was so nearly negligible that the vent condenser was removed for retubing and the plant operated without exceeding the manufacturer's original guarantee of 14 pounds of solvent per ton of seed.

If properly designed, the air handling or vent system will serve to minimize solvent loss in other ways. Each vent line should be sized sufficiently large to carry the entire vapor flow from the equipment it serves. The vent condenser should be sized large enough to condense the normal vent load plus the vapors from any other individual condenser. In this way pressures will never build up in the vessel, and vapors from the vessel will always pass through the



EFFECT OF TEMPERATURE & SOLVENT ON RATE OF EXTRACTION OF COTTONSEED FLAKES 0.016" THICK.

vent system. If the water flow through any condenser is interrupted, the vapors from that condenser will pass to the vent condenser and be condensed, preventing loss.

There are two principal ways by which steam may be wasted: by leaks in piping and equipment and by excessive process demands. Since the first is a common maintenance problem needing no discussion, only the second will be discussed here.

Almost all process steam is used for vaporizing hexane from the extracted oil and spent flakes. Therefore a logical way to reduce steam consumption is to pump less hexane; that is, reduce the solvent ratio. To the superintendent selecting a new plant, this means choosing an efficient extractor, one making the best use of the solvent supplied it. To the superintendent operating an existing plant, this means substituting, insofar as possible, thin flakes and high extraction temperatures for high solvent ratio. Ordinarily the system with the lowest solvent ratio will have the lowest steam demand.

The steam consumption in many of the older plants also can be diminished by reducing the amount of blowing or direct steam used for final stripping of both oil and meal. In most of the older plants there is no accurate measurement of these two flows and, as a result, an excess is frequently used.

Water requirement in general follows steam requirement rather closely. Many plants using a large amount of steam will also use a large amount of water, and any reduction in steam usage can be followed by a reduction in water usage, provided proper attention is given to discharge water temperatures.

5. *Operating safely.* The plant which is well maintained, which has a minimum of leaks, and in which the housekeeping is good, automatically tends to be a safe plant.

Mention has already been made of the importance of the vent system in minimizing solvent loss. Where flammable solvents are used, this same vent system is of considerable importance from the safety standpoint. If the system is designed with each vent large enough to carry all the vapors from the equipment it serves to the vent recovery system, the tendency to lose solvent inside the plant is greatly diminished. As a result, there is little possibility of building up significant concentrations of vapor in the extraction area.

Choice of proper electrical equipment and controls also can have an important bearing on safety where flammable solvents are used. Almost every major fire in the solvent extraction industry in this country has been caused first by a build-up of flammable vapors and second by an electrical spark. Spark-proof motors and controls should be used not only in the extraction area but also in any adjacent area where there is a possibility of vapors concentrating. The electrical control room should either be spark-proof or should be situated so as to prevent entry of flammable vapors. This can be accomplished either by sealing the room and drawing air from a safe point, or by locating the room at a point where contamination is not possible. With the vent system completely engineered to prevent discharge of hexane except at a preselected point and the possibility of sparks prevented wherever hexane might conceivably collect, the risk due to fire and explosion is extremely slight.

It should be made clear that explosion and fire are not the only hazards in solvent plants. Probably more injuries and lost time have resulted from the usual industrial accidents than from fires.

In the designing of these plants economic pressure is always present. There is always temptation to reduce cost by omitting such so-called niceties as access ladders, working platforms, and guards. Resisting this temptation is the particular responsibility of the superintendent. He has a responsible position, and his opinions are well respected by his management. He should insist that proper safety features are included in the design. The small added cost for such safety features will be justified many times over by prevention of down time of equipment and lost time of experienced operators.

[Received January 2, 1951]

Studies of the Spectral Characteristics of Alkali-Isomerized Autoxidized Fatty Acids[1,2,3]

ORVILLE S. PRIVETT and W. O. LUNDBERG, The Hormel Institute, University of Minnesota, Austin, Minnesota

THE presence of small amounts of nonconjugated trienoic and tetraenoic fatty acids in certain oils, detected by spectrophotometric methods but not detectable by chemical methods, has been questioned (2, 4). Hilditch and Shrivastava (2) were unable to confirm spectrophotometric analyses of linolenic acid in a number of common seed oils by a refined chemical procedure and suggested that the slight conjugated triene absorption developed during the alkali isomerization might be caused by any one of a number of extraneous factors. Swain and Brice (4) showed that small amounts of conjugated triene and tetraene formed during the alkali-isomerization of autoxidized linoleic and linolenic acids, respectively. They suggested that the conjugation produced in the products of autoxidation during the alkali-isomerization could be estimated by a spectrophotometric examination of the sample after heating in neutral ethylene glycol. However a careful examination of their results indicates that the procedure does not afford a quantitative means for estimating the spurious conjugation formed during the alkali-isomerization treatment.

[1] This study was a necessary preliminary to the work specified in a contract sponsored by the Bureau of Human Nutrition and Home Economics, U. S. Department of Agriculture, and authorized by the Research and Marketing Act of 1946.

[2] Presented at the fall meeting of the American Oil Chemists' Society, San Francisco, 1950.

[3] Hormel Institute publication no. 57.