COMMERCIAL SOLVENTS FOR SOLVENT EXTRACTION

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Activity in connection with the solvent extraction of oil seeds has been particularly marked, of late, in the United States. This method has been widely and successfully adopted in Europe for the last ten or twenty years but comparatively little is known in the United States in connection with the practical application of different solvents. The use of the proper solvent is essential for the successful operation of such a plant, and in the past 25 years solvent extraction plants for oil seeds in the United States have frequently been unsuccessful, either because of the inability at the time they were constructed to obtain a proper solvent or because of ignorance as to which to use. This condition no longer obtains and a variety of useful solvents may without difficulty be procured in the United States, upon the open market.

This paper will discuss the physical constants of the most important of the solvents and their usefulness in commercial application as judged from experience in solvent extractor plants in the United States and abroad.

Requisites of a Solvent

The first requisite of a solvent for commercial extraction of oil seeds is evidently that it dissolve the oil. Certain products described below are excellent for this purpose but have the additional tendency to dissolve color from the seed, which is an undesirable feature.

The second condition is that the solvent be easily vaporized and homogeneous in composition, so that with facility, it can be removed completely by steaming from the oil and the extracted residue.

A third requisite is that the entire solvent distill at a temperature below 212°, in spite of the fact that a higher boiling solvent will vaporize at a lower temperature in the presence of water vapor. "Heavy Ends" are extremely difficult to remove from the residual meal, and the attempt to use solvents possessing them, in the past, has given the impression to those not familiar with modern extractor practice that the oil and meal cannot be entirely deodorized from the solvent. The hundreds of plants in operation primarily in Europe have demonstrated conclusively that this is easily accomplished in a correctly designed system and provided a solvent with the proper boiling range is used.

The fourth requisite is that there be no "light ends." These products are difficult to condense, will eventually be lost and, in the case of inflammable solvents, increase the fire risk. In addition, they may be injurious to the health of the operators as uncondensed vapor in the atmosphere of the plant, although in a properly operated solvent extraction there should be no odor whatever of solvent.

The fifth consideration is the relative fire hazard. The explosion risk is negligible, since in reality there are very rarely explosions within an extractor, since the exact quantity of air and solvent vapor must be encountered. Such explosions as have occurred have generally been steam explosions, caused by too great pressure of steam within a still or extractor. This can evidently be obviated by proper design.

Description of Various Solvents

Solvents may be classed in one of three categories:

Inflammable Solvents:	Petroleum Ether Gasoline (motor fuel) Special cut of gasoline Ether Benzol
Semi-Inflammable Solvents:	Ethylene Dichloride Trichlorethylene 75%—Benzol 25% Mixture Carbon tetrachloride 30%—Gasoline cut 70% Mixture
Non-Inflammable Solvents:	Trichlorethylene Carbon tetrachloride

Petroleum Ether: For use in commercial extraction plants, the product which is known in the laboratory as petroleum ether is not interesting except in special cases. Its boiling point is so low that it is difficult to condense and therefore the loss is unduly high. In view of its high cost, this removes it from practical consideration for the extraction of oil seeds.

Gasoline: Gasoline such as is used for motor fuel is not suitable for the extraction of oil bearing seeds without further refinement. The term "gasoline" is used somewhat loosely for any cut from low boiling petroleum products. The terms naphtha and benzine are also frequently employed but are merely trade names for slightly different types of gasoline.

The unsuitability of motor fuel gasoline for the extraction of edible oil will be appreciated by an examination of the average analysis of 1,049 samples collected by the Texas Company, and given below.

Per cent by Vol.	Av. 1049 samples	Govt. Specifications	Sample A Motor fuel	Sample B special	Sample C special
Initial B. Pt	114°F	141	88	107	80
20%	208	221	187	...	..
50%	277	284	260	...	..
90%	378	392	355	...	..
End Point	431	437	396	328	212

There has also been included three samples of gasoline products obtainable upon the open market, and the U. S. Government specification for a motor fuel.

It will be seen that the "heavy ends" of gasoline in extracted oil or meal would require intensive steaming which is not only wasteful of steam but is the principal cause of an extracted meal or oil possessing a solvent odor. It may be considered axiomatic therefore that for practical solvent extraction plant operation, no solvent should be used if any portion of it boils over 212°F. It might also be added that it is not advantageous to have any product boiling below 125° F.

Special Cut of Gasoline: On the European market there is easily obtainable a special cut of gasoline made from the American product by the refineries in Europe with the following specifications:

Boiling Point	122°F
2%	140°
97%	194°
End Point	200°

This product is the ideal solvent from the standpoint of the quality of oil produced. It has been produced in the United States at individual extraction plants from good quality gasoline similar to Sample A listed above. Although the boiling points indicated for the sample would not appear to make it possible to obtain half of this gasoline in the form of a rectified solvent similar to the special cut mentioned above, it nevertheless is a fact in practise, as the writer has observed from his own experience. It must be remembered that the boiling points shown above were determined in the laboratory in a simple distillation apparatus without a rectifying column, and are therefore empiric.

It might be of interest at this point to briefly describe a simple and inexpensive type of rectifying apparatus which produced this product.* A kettle still equipped with steam coils and direct steam was surmounted by a 8″ pipe 6′ long which was filled with small glass rings, thus resembling a Hempel column. These glass rings were made from glass tubing cut to short lengths and may be obtained commercially at a cost of approximately $25.00 per cu. ft. A dephlegmator was attached to the rectifying column and an excellent clear-cut product produced which was even better in quality, in the opinion of the writer, than could have been obtained with a bell and collar type of distillation column occupying the same space or costing the same to install.

Ether: Ether is not a solvent suitable for the extraction of oil

* Chemical and Metallurgical Engineering, January 3, 1923.

seeds because of its high cost and the difficulty experienced in condensing it without undue loss.

Benzol C_6H_6:

Boiling Point	176.0 °F
Freezing Point	42 °F
Specific Gravity at 68°F	0.878
Latent Heat	92.9 Cal.
Boiling Pt. Benzol—water mixture	155 °F

This product is one of the easiest to obtain and most satisfactory solvent for many substances. Its disadvantage lies principally in its tendency, in common with the other aromatic series of solvents, to dissolve some color from certain seeds, and thus produce a darker oil than that obtainable with the special gasoline cut mentioned above.

The price is approximately the same as gasoline and its distillation range should not be more than 4°F, one of the points being its boiling point of 176°F. It is therefore an extremely pure compound which is easy to distill and condense. It is consequently extremely easy to eliminate all traces of this solvent from the oil and meal. It should be thiophene free.[1]

It is possible that a satisfactory and very cheap solvent can be derived from the "Light Oil" manufactured at the benzol plants of coke-oven and gas works. The cut known as "raw benzol" boils between 140°F. and 230°F. It is only during the last four hours of a twenty hour distillation in the raw benzol still that any products are produced boiling over 195°F. Therefore it would be possible to cut the distillation at this point and to throw all of the products above 195°F. into the raw toluol fraction. This would produce a solvent with the proper boiling point, but the degree of necessary refining would have to be determined from experience of extracting with the above product. The writer does not know of instances where this product has been employed for extraction, but offers it as a suggestion as a possible low cost solvent.

Semi-Inflammable Solvents

Ethylene Dichloride[2] $CH_2Cl\text{-}CH_2Cl$.

Flash point (open cup)	60°F
Fire point	90°F
Specific Gravity at 68°F	1.2569
Boiling Pt.	182°F
Freezing Pt.	—32°F
Specific Heat	0.3054 at 86°F
Heat of vaporisation	157.5 BTU per lb. at 32°F

This compound has been variously known as "Dutch Liquid"

[1] To test for this product qualitatively, place a few crystals of isatin in a shallow porcelain dish previously rinsed with sulphuric acid. Add 0.5 cc. sulphuric acid and 5 cc. benzol. Cover with watch glass and allow to stand 30 minutes. If blue rings occur around the isatin, thiophene is present.—Lunge-Kohler, Steinkohlenteer & Ammoniak, Vol. 1.

[2] The information contained herein is based upon that furnished through the courtesy of the Carbide & Carbon Chemical Co., and that contained in the article on ethylene dichloride in Chemical & Metallurgical Engineering, Vol. 25, No. 22, Nov. 30, 1921.

"Elaychloride" "Ethylene Chloride" or by the more exact term "1, 2-dichlorethylene."

This is intermediate between inflammable products such as have been described above and the non-inflammable or fire extinguisher products such as trichlorethylene and carbon tetrachloride over which it is claimed it has the advantage of hydrolysing to a less extent. Its inflammability is low since it requires a concentration in air of 6.2 per cent before the lower explosive limit is reached, whereas the lower explosive limit of ether in air is 1.71 per cent, benzol 1.41 per cent and an average gasoline 1.5 per cent. Looked at from one point of view, it may therefore be considered as having one-quarter the tendency to explode as these inflammable products. However it should be noted that ethylene dichloride air mixture cannot be exploded by a spark but requires an open flame at least 1 or 2 inches in length to start the explosion which is a feeble one. The product possesses a characteristic odor similar to chloroform and trichlorethylene and it is quite certain that its presence in air would be detected by the sense of smell long before its concentration approaches the 6 per cent mark. Its inflammability is not great, since, although it will burn, a draft of air created by the heat is sufficient to extinguish the flame. Due to the fact that it is heavier than water, it may be extinguished by water in contradistinction to benzol or gasoline.

With a solvent such as ethylene dichloride, the writer does not believe that there is any real fire or explosion hazard in connection with any recognized widely-adopted extraction system. However it would appear as an important step on the part of the manufacturers of this product for them to settle the matter definitely from the insurance underwriter's standpoint, since the principal advantage of an expensive solvent such as this (costing $0.10 per pound, or $1.07 per gallon) is the lowest insurance rate that should be obtainable. Also the authority should be obtained to utilize such a product within the limits of large cities.

Trichlorethylene 75 Per Cent—Benzol 25 Per Cent Mixture: This mixture is a semi-inflammable and similar in this respect to ethylene-dichloride. Its main advantage lies in the fact that the cost of benzol is approximately one-quarter that of trichlorethylene and therefore the cost of the mixture is less than the pure trichlorethylene. The writer does not know of any extraction plants using this mixture.

Carbon-tetrachloride 30 Per Cent—Special Gasoline Cut 70 Per Cent Mixture: This product is similar to the mixture mentioned above. The tendency for the carbon tetrachloride to hydrolyze precluded it from use with steel or iron apparatus. Margosches and Braunlich[1] and Merz[2]

[1] Margosches. Der Tetrachlorkohlenstoff, Stuttgart, 1905.
[2] Fritsch, Fabrication et Raffinage des Huiles Vegetales, 1922.
[3] Much of the technical data on this substance has been supplied through the courtesy of Roessler and Hasslacher Co.

maintain that such a mixture is impossible to use commercially because of its tendency to fractionally separate during distillation.

Non-Inflammable Solvents

Trichlorethylene[3] $CHCl:CCl_2$

Boiling Point	190.4°F
Freezing Point	94°F
Vapor tension at 77°F	56 mm
Latent Heat (Cal.)	56.6 Cal.
Specific Heat at 64.4°F	0.233
Specific Gravity at 77°F	1.460

This product may be classed as absolutely non-inflammable and may be used as a fire-extinguisher liquid. It is used to a considerable extent for the extraction of various materials including oil-seeds. Because of its gravity the current of solvent should, if possible, pass upward through the mass of seed since the solution of oil and solvent has a slightly lower specific gravity than the pure solvent and therefore has a tendency to rise to the top.

It formerly was manufactured abroad only and the duty of 35 per cent brought its cost to over $0.11 per pound. It is now being produced in the United States, and is sold at a price (at the present writing) between 8½c and 9c per pound. This makes its cost per gallon (12.28 lbs.), $1.05 to $1.10 in large quantities.

This product, it has been stated, has the disadvantage of hydrolyzing sufficiently to cause damage to steel extraction apparatus. The writer has visited numerous European extraction plants which have used trichlorethylene for a number of years, and the managers have assured him that they have not been troubled with corrosion. Edouard Bataille, a manufacturer of extraction machinery, has remarked the same favorable results in the many plants which he has installed in the past thirty years, many of which use this solvent.

In order to determine the comparative action upon different metals, pieces of the various substances were heated over a period of five days in trichlorethylene and water, to observe the effect of the resulting hydrolysis. The results were as follows:

	Per cent loss of weight
Wrought Iron	0.04 %
Cast Iron	0.04 %
Copper	0.03 %
Lead	0.015%

According to this result it would have taken approximately 34 years of constant attack to have corroded the wrought iron in its entirety.

Another series of tests is reported where thin strips of metal were exposed to the action of trichlorethylene and moisture by being placed in a reflux condenser for 10 hours. One set of experiments was made with oil seeds present in the solvent to observe the effect of the presence of free fatty acids and the other with the solvent and moisture alone. The results are reported in loss of weight per 0.5 sq. inch of surface exposed:

	Mild Steel	Wrought Iron	Nickel	Aluminum	Lead
Trichlorethylene with water	Slight	Slight	Nil	Nil	Nil
Trichlorethylene water and oil seeds	0.0025 gm.	0.0028	Slight	Slight	0.0010

Carbon Tetrachloride CCl_4

Boiling Point	170 °F
Freezing Point	–9.4°F
Specific Gravity at 77°	1.583

This non-inflammable solvent has been rejected for use with steel solvent extraction apparatus because of its marked tendency to hydrolyze. It has been recommended that the hydrochloric acid can be neutralized by the addition of a small amount of hydrated lime in the bottom of the still but this is evidently impossible to do in the distillation of the solvent from vegetable oils.