# A Review of Oleoresin Black Pepper and Its Extraction Solvents

By J. S. Pagington, C. Chem, MRSC, FIFST

Spice oleoresins, which are the solvent extracts of spices, have been used in the food industry for over twenty years. They became accepted during the 1970s as a common ingredient for the food manufacturer and their production and consumption have been steady over the last few years. Extracted spices which are often spread onto a salt or cereal base offer the food manufacturer a clean and standardised form of what was once a variable and a dirty ingredient.

At least 50% of the world production of spice oleoresins is represented by black pepper oleoresin, most of which is consumed in the U.S.A., U.K., Canada and W. Germany. When they were first introduced, oleoresins were manufactured in the user countries, i.e., U.S.A., Canada and U.K., however the trend has been for the producing countries to set up their own oleoresin plants, often with the backing of companies from America or Europe. Currently the U.S.A. imports around 60% of its oleoresin pepper requirements, whereas the U.K. only imports 10%.

Manufacturing plants are starting up in India, Indonesia, and Malaya at the rate of several each year. Most, if not all, have little knowledge of their intended market or of its current or proposed legislation and how it may affect their

**The Author—J. S. Pagington, formerly Technical Manager with The British Pepper & Spice Co., Ltd., now represents P. T. Polind of Tanjungkarang-Timur, Indonesia, on a worldwide basis. He has worked with spices, seasonings and oleoresins for the last fourteen years and during 1982 has been responsible for the conversion of P. T. Polind's oleoresin plant to alcohol extraction.**

products. There are a number of plants around the world which have never produced or sold more than a few kilos of oleoresin. The result of this is a considerable overcapacity worldwide for oleoresin production. It is however very difficult to find a consistent supply of the right product which will conform to the users' specification and to the importing countries' legislation.

Three solvents have been used in the manufacture of oleoresin black pepper. In the U.K. acetone and dichloromethane (methylene chloride) have always been the preferred solvents. In countries where the ambient temperature is high it is not always practical to use methylene chloride, and dichloroethane (ethylene dichloride or EDC) is used as well as acetone. Both hexane and methanol are used for some spices but not pepper.

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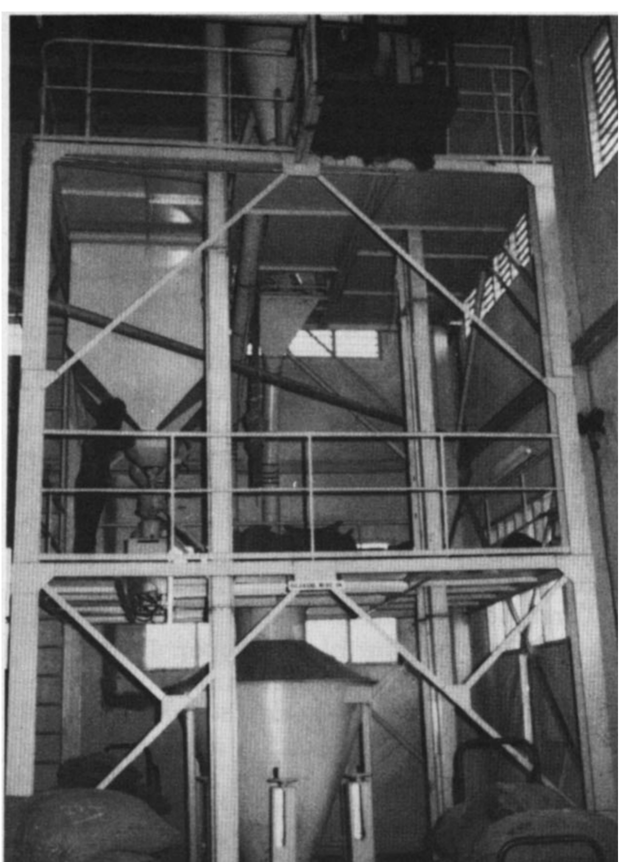
An extraction solvent should exhibit the following properties:

- Be acceptable as a food solvent
- Leave no harmful residues in the food product
- Be able to be removed down to very low levels without harming the product, e.g., by vacuum distillation or an azeotropic system or both
- Readily dissolve the desired flavouring ingredients while leaving the fibre, cellulose, and starch sugars of the plant in the insoluble residue
- Be easy to remove by distillation and economical to recovery

### Acetone

Acetone has long been accepted as a food solvent, and in 1978 was classified as a Group A solvent by the U.K. committee on Toxicity of Chemicals in Food, in the Food Additives and Contaminants report on solvents (FACC).[1]

Group A solvents are defined by that committee as "substances that the available evidence suggests are acceptable for use in foods." No maximum residual levels were specified, but a purity criterion was recommended, i.e., "provided the specification includes a limit on mesityl oxide." In the same report a maximum mesityl oxide content in acetone of 10 ppm was recommended.



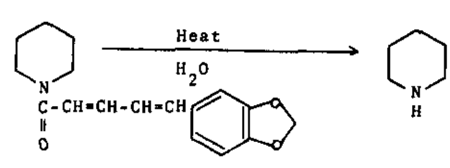
Pepper grinding operation

In Europe the EC Scientific Committee for Food is currently examining the safety-in-use of solvents. In their earlier proposals acetone was listed as being acceptable for the extraction of fats and oils, cocoa butter and natural flavouring materials.[2] These proposals have now been updated and conditions of use are no longer specified.[3] A residual level of 5 ppm in the food delivered to the ultimate consumer is recommended.

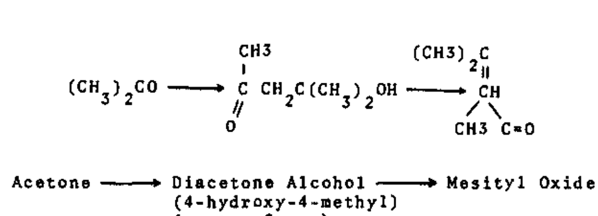
Both the American regulations[4] and the Canadian regulations[5] limit acetone residues to a maximum of 30 ppm in spice oleoresin.

Providing that it is free of mesityl oxide, acetone is a safe and acceptable solvent. Unfortunately, it is possible to produce mesityl oxide from acetone during the removal of the solvent from the oleoresin.

Under certain conditions the refluxing of oleoresin pepper in the presence of water (from a water soluble solvent, e.g., acetone or ethanol) will convert some of the piperine present to the base piperidine.

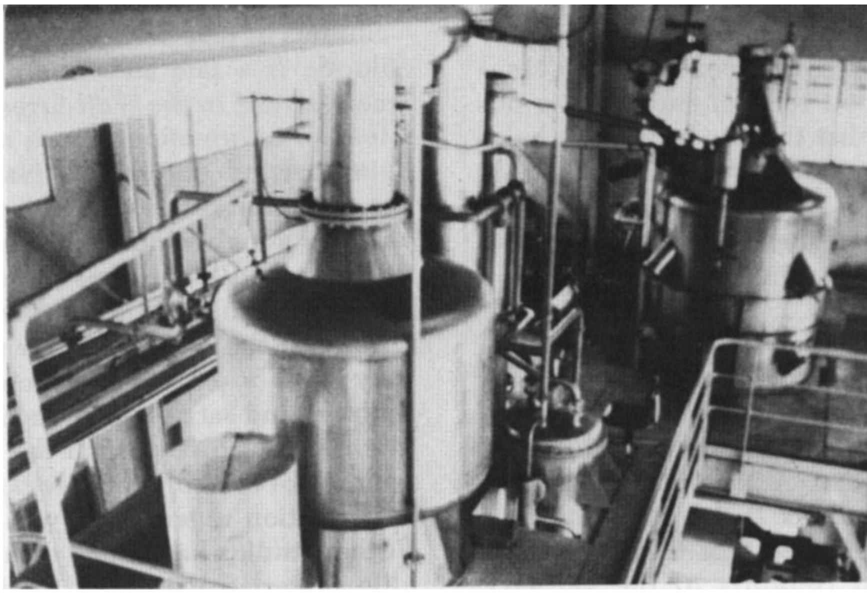



This reaction is sufficient to raise the pH and make the oleoresin basic thus facilitating the conversion of acetone to mesityl oxide via diacetone alcohol.




Analysis of some acetone extracted pepper has revealed mesityl oxide levels as high as 340 ppm, whereas in others it cannot be detected. Analysis also indicates a large variation in residual acetone from 20 ppm to 1,000 ppm (0.1%).

The use of acetone for the extraction of pepper



**This photo shows the extraction vessel and first stage evaporation.**

can present problems for producers both in terms of residual solvent levels and contamination from mesityl oxide which can become a serious problem for the meat manufacturer. The reaction between parts per billion of mesityl oxide and the hydrogen sulphide present in meat is well documented,[6-8] and the resulting catty odour produced (attributed to 4 methyl-4-mercapto-pentan-2-one) is well known to many meat processors. Over the last few years concern about mesityl oxide has led to many manufacturers' refusal to accept acetone extracted pepper. It has, therefore, become necessary to find an acceptable alternative to acetone, at least for black pepper extraction if not for the other spices.

### Methylene Chloride

Used by companies in both the U.K. and U.S.A. methylene chloride is a well tried and tested solvent for oleoresin pepper. The low boiling point of methylene chloride (40.2°C) necessitates the use of refrigeration to condense it, and in countries where the ambient temperature can rise above 30°C, the handling of methylene chloride is extremely difficult if not impossible.

In 1978, the U.K. FAC committee classified dichloro methane as a group B solvent, i.e., "Substances that on the available evidence may be regarded meanwhile as provisionally acceptable for use in food, but about which further in-

**Table 1.** Chemical and Toxicity Data for Some Solvents

| | Molecular Weight | Chemical Formula | Boiling Point Degrees C (760mm) | Density at 20 Degrees C Kg/Litre | TLV(3) ppm | LD50(4) 5 kg |
|---|---|---|---|---|---|---|
| Acetone(1) | 58.08 | $(CH_3)_2CO$ | 56.20 | 0.7911 | 1000 | 19.7 |
| Methylene Chloride (2) | 84.94 | $CH_2Cl_2$ | 40.20 | 1.3200 | 100 | - |
| Ethylene Dichloride (1) | 99.00 | $CH_2Cl\ CH_2Cl$ | 83.50 | 1.2550 | 50 | 0.7 |
| Mesityl Oxide(1) | 98.14 | $(CH_3)_2C{=}CH(CH_3)CO$ | 128.30 | 0.8569 | 25 | - |
| Ethanol(1) | 46.07 | $CH_3CH_2OH$ | 78.32 | 0.7904 | 1000 | 113.7 |

(1) Organic Chemicals Date Book, BP Chemicals (UK) Ltd., Second Edition, 1970

(2) Methylene Chloride. The Powerful and Versatile Solvent. Publ. by Imperial Chemical Industries Ltd.

(3) Threshold Limit Values (TLV) for chemical substances in workroom air.

(4) Lethal Dose 50% (LD50) is the amount of material, applied as a single dose, which causes death in 50% of the subjects so treated. It is quoted as grams of the material per kilogram of body weight.

formation is necessary and must be reviewed within a specific time."[1] At the same time results were requested of an oral carcinogenicity study in the rat within five years and a provisional limit of 5 ppm in food recommended. It is understood, however, that this study has not been carried out, and the ministry will accept the evidence of inhalation trials on the basis that methylene chloride follows the same metabolic route from both the lung and stomach.

In December 1980, ICI, the manufacturer of methylene chloride in the U.K., issued a circular[9] following a collaborative study to investigate the long term effects of exposure by inhalation of rats and hampsters to methylene chloride. The circular stated that "A preliminary analysis and review of all findings at the completion of exposure has now revealed that there is an increase of malignant tumours of the salivary gland in exposed animals when compared to controls." In 1981 the TLV value for methylene chloride[10] was reduced from 200 to 100 ppm.

In Europe the EC Scientific Committee for Food (1975) listed its use for the decaffeination of coffee and extraction of natural flavouring material.[2] By March 1981 a recommendation had been included placing a maximum of 10 ppm in tea and coffee and 2 ppm in flavourings prepared from natural flavouring materials.[3] The commission has also included dichloro methane in the list of solvents to be re-examined within five years. Both the American regulations[14] and Canadian regulations,[5] limit methylene chloride residues to a maximum of 30 ppm in spice oleoresins.

Studies to date have indicated that methylene chloride is a safe and acceptable solvent.[11,12] A recent article in the *Wall Street Journal*[13] reports a leak of information from a major investigation being carried out by the National Institute of Environmental Health Sciences. This report suggests a high incidence of liver cancer in mice that were fed high doses of methylene chloride. The final results of these trials will not be available until the end of 1983, and it is hoped that they will be conclusive enough to settle the problem and satisfy the legislators.

It is clear however that the concern about the banning of this solvent may be well founded and the situation regarding it will not be clear until further studies have been completed. The use of chlorinated solvents in food evokes a strong reaction from some people, and many users share the view that the day must come when they will no longer be permitted to use chlorinated solvents.

### Ethylene Dichloride

EDC was classed as a group B solvent by the U.K. FAC committee,[1] a maximum level of 5 mg/kg in food was recommended and the results of an oral carcinogenicity study in the species other than rat was requested to be completed within five years.

In Europe the EC Scientific Committee in-

The P.T. Polind Factory

cluded EDC in its 1975 listing for decaffeination of coffee and extraction of natural flavouring materials.[2] However by January 1981 this solvent had been dropped from the list.[3]

The American regulations currently limit ethylene dichloride to a maximum of 30 ppm in spice oleoresins.[15] However, the Department of Health and Human Services' Second Annual Report on Carcinogens indicates that the FDA may act "to eliminate residues of 1, 2 dichloroethane in food."[16] HHS state that the solvent had been labeled an animal carcinogen and that the agency has initiated revocation of the regulations including the section which clears it for spice extraction.

During 1982 the Canadian Food and Drug Regulations have been amended to revoke the use of EDC as a solvent for extracts.[17] Most oleoresin pepper coming into the U.S.A., Canada and Europe from India, Indonesia, and Malaya will be EDC extracted material. When this legislation restricting EDC is introduced, and this seems likely in Europe as well as the U.S.A. and Canada, it will create a serious problem to many suppliers and importers.

### Alternative Solvents

In the light of the above comments, any alternative solvent should conform to all the five points listed as desirable for a solvent and also leave either no residue in the food or a residue which is entirely acceptable. Two solvents readily fall into this category, carbon dioxide and ethyl alcohol.

### Carbon Dioxide

Much has been published about this exciting new solvent. The extraction of natural products with both liquid and supercritical carbon dioxide is already a practical reality as hops and coffee are now being extracted in quantity in various parts of the world.

The extraction of black pepper has also been carried out on a laboratory scale by several workers.[18,19] The technique looks very promising, offering a flexibility to separate oil, chlorophyll and piperine which cannot be achieved by conventional solvent extraction. The scaling up of such a plant to produce commercial quantities of oleoresin indicates a capital investment of at least twice that of a conventional solvent extraction plant. While the extraction technique is very new, the technology involved is not and, therefore, a dramatic drop in capital cost is not to be expected over the next few years. This is unfortunate, but it seems that it will be some time yet before carbon dioxide extracted pepper can be available at an economic price.

### Ethyl Alcohol

Laboratory work has shown that ethyl alcohol behaves very much like acetone in a conventional extraction plant. Providing that ethyl alcohol can be purchased free of duty then it can be an economical alternative and can give a good yield of an acceptable oleoresin.

Residual levels of ethyl alcohol should not cause any problems and levels of up to 1% can be left in the oleoresin if required. This will produce a far more mobile resin which would be easier to spread on a base, and it will take away the need to heat the resin to very high temperatures in order to remove final traces of solvent.

Ethanol is acceptable in Europe, Canada[5] and the U.S.A.[20] where it is classed as GRAS. It is not felt that any maximum residual levels would be imposed in spice extracts, other than levels above which excise duty is payable.

By the end of 1982 the first large scale pepper extraction plant using ethyl alcohol as a solvent will be in production. Product from this plant will be available in both North America and Europe, and will not be affected by whichever way the legislation may go in the next few years.

The plant, which is based in Indonesia, was constructed two years ago to extract pepper with dichloroethane. Work on conversion of this plant to use ethyl alcohol is now complete and the initial results are very encouraging. Problems of moisture and oil build-up in the solvent have been overcome and solvent recovery figures similar to those for EDC are being obtained.

All the indications are that an oleoresin pepper can be produced at a similar cost to the products now on the market. The physical appearance of this resin may differ a little from the conventional product, but its organoleptic properties are superior in that it lacks the sweet taste and aroma which is so characteristic of chlorinated solvents.

**References**


1. Food Additives and Contaminants Committee Report on the Review of Solvents in Food. FAC/REP/25. HMSO 1978.
2. Proposal for an EEC Directive on Solvents for Use in Food. Paper 3186/V1/75-E
3. Proposed EC Directive on Extraction Solvents. Working Document 111/987/80-EN
4. Code of Federal Regulations. 21 CFR 173.210
5. Canadian Food and Drug Regulations. Section 16 Table XV
6. J. I. Anderton, J. B. Underwood. Catty Odours in Foods: BFMIRA Technical Circular No. 407, September 1968
7. R. Spencer. A Layman's Guide to Catty Taints in Food. BFMIRA Review, August 1969
8. N. Goldenberg, H. Matheson. Off Flavours in Foods. A Summary of Experience 1948-1974. Environmental Health, March 1976, 84 (3) 63-8
9. ICI Circular Ref: PLW/CEM 11 Dec. 1980
10. Threshold Limit Values for 1978. HSE Guidance Note EH 15/78
11. Friedlander, Hearne & Hall, Epidemiologic Investigation of Employees Chronically Exposed to Methylene Chloride. Occup. Med. 20.657-666 1978
12. Hearne and Friedlander. Letters to Ed. Occup. Med **23**(10) 660 1982
13. Anon. Process to Remove Coffee's Caffeine May Use Carcinogen, Wall Street Journal, June 18 1982
14. Code of Federal Regulations 21 CFR 173.255
15. Code of Federal Regulations 21 CFR 173.230
16. Report of the Department of Health and Human Services. Second Annual Report on Carcinogens. Food Chemical News. May 10 1982
17. Canada Gazette **116** (8) 28/4/82, 1541
18. British Patent 1336511 1973
19. P. Hubert, O. Vitzhum. Fluid Extraction of Hops, Spices and Tobacco With Supercritical Cases. Angew. Chem. Int., Ed. Engl. 17, 710-715 (1978)
20. Code of Federal Regulations 21 CFR 184.1293