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cc: JNH / DEC - Brussels
C PATON - St. Louis

SUBJECT DIPHENYL FOR CITRUS FRUIT PRESERVATION.-

REFERENCE SR/Lcd

TO GF FAGUE - St. Louis

Attached is a copy of Diphenyl Literature for the application as a Citrus Fruit Preservative. Please arrange its toxicological and legal clearance.

In order to prepare drafts for other Diphenyl applications, I would appreciate if you sent me a toxicity statement for this product.

S ROEHR

Attachment

BELS/G-86

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DIPHENYL
for
CITRUS FRUIT PRESERVATION

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DIPHENYL FOR CITRUS FRUIT PRESERVATION

Introduction

Since the observation by Tomkins in 1935 that diphenyl (biphenyl) is effective in reducing decay in citrus fruits and other fruits and vegetables, considerable effort has been directed towards making practical use of it in the citrus industry. In the early work in Palestine, dated as far back as 1935, paper impregnated with diphenyl was used to wrap the fruit. Spoilage was reduced from 54% in the controls to 5.4% in the diphenyl wraps. A patent (U. S. 2,265,522) on diphenyl wraps for the preservation of citrus fruit was obtained by Farkas.

In experimental studies carried by the Florida citrus experiment station, Lake Alfred, Florida, diphenyl wraps and diphenyl box lines were found to greatly reduce both stem-end and rot and mold when compared with unwrapped controls and fruits in ordinary wraps. Oranges kept in diphenyl box lines for one week and then removed still showed enough less decay than the controls at the end of three weeks to constitute a good degree of control.

The success of diphenyl has been amazing through extensive tests of paper lines treated with this highly successful decay deterrent. The quartermaster of the Army specified diphenyl treated lines for one half million boxes of fresh Florida citrus fruits purchased for overseas troops in 1945 to 1946. This is a non-regular practice.

Crown-Zellerbach's U. S. Patent No. 2,173,453 covers the use of biphenyl in tissue wraps for oranges. Within the patent specifications the quantity of diphenyl for each tissue wrap weighing approximately 1.4 grams, is 25-42 mgs.

It is our understanding that diphenyl is mixed with paraffin wax in equal ratio and the application to the tissue paper is made by passing the paper through a bath containing the molten diphenyl and paraffin, followed by squeezing between a set of rolls.

Methods of Application

Generally, there are four methods of application of diphenyl:

1. Tissue wrap.
2. Treated boxes or collars.
3. Liners, top and bottom, or the side panels.

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4. Paper liners for Bruce boxes. The latter are sometimes used for storage or export.

Orange boxes for export require two liners, each (11.5 x 12) 2 x 24 square inches equals 7.8 square feet per liner or 15.6 square feet of diphenyl treated paper per box. Each square foot of paper is coated with 0.00283 pounds of diphenyl along with a like amount of wax materials--either paraffin wax alone or a mixture of paraffin wax and petrolatum. Accordingly, each orange box require 0.044 pounds of diphenyl for the two liners in the box.

Method of Impregnation

The method employed for applying diphenyl to paper is largely a matter of individual preference, the aim being to produce a paper containing the correct amount of diphenyl. The following general considerations should, however, be borne in mind.

(a) Diphenyl is extremely volatile and has a strong aromatic odor. Hence, the lower the temperature of application the less will be the losses of preservative during processing.

(b) If maximum preserving efficiency is to be achieved, there must be no significant loss of diphenyl from the paper before it reaches the fruit packer. Diphenyl is a crystalline material having little natural adhesion to paper. The use of some vehicle to bind the preservative to the fibres of the paper is, therefore, recommended if flaking-off during handling is to be avoided.

The four main methods of impregnation will now be considered in turn.

1. Direct Application

Diphenyl alone is used.

Diphenyl is heated to 70°C. (160°F.) in order to melt the diphenyl. The paper is impregnated by rolling in the preservative by means of heated rollers. In view of the difficulty of obtaining a sufficiently thin coating, it us usual to apply the diphenyl in the form of stripes or dots in such a pattern that the average diphenyl content per unit area is maintained.

2. Vapor Application

Diphenyl is used alone or in conjunction with paraffin wax, which stabilizes the preservative by preventing the premature evaporation of the diphenyl.

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British Patent 525302 (lapsed) does for instance give diagrams of suitable boilers in which diphenyl and paraffin wax are vaporized and diluted with steam or an inert gas. This mixture is then projected on to the paper to give a uniform distribution of the preservative which solidifies on, or just before, contact with the cold paper.

3. Wax Coating

Diphenyl	50 parts by weight.
Paraffin Wax	50 parts by weight.

The above mixture is heated to its melting point and applied to the paper by means of a heated roller. The paper is then passed through a series of heated nipper rollers to ensure a good bond between the coating and paper. The object is to coat the paper at the recommended rate per unit area; the actual depth of impregnation is not so important because the preservation of the fruit is achieved by vaporization of the diphenyl from the coating during storage. The temperature of the diphenyl and paraffin wax mixture should not be allowed to exceed 70°C. (160°F.) as a higher temperature will cause considerable loss of diphenyl by vaporization.

4. Warm Solvent Application

(a) Diphenyl--25 parts by weight.
Medicinal grade Liquid Paraffin--75 parts by weight.

The liquid paraffin should be a non-toxic, odorless and tasteless grade (such as 'Liquid Paraffin B.P.').

The diphenyl and liquid paraffin are warmed together at 40°C. (104°F.) and this temperature is maintained throughout application. Below this temperature, diphenyl tends to crystallize from the solution.

The solution is applied by the usual roller coating technique for coated papers.

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Equipment

Existing waxing or printing equipment can generally be adapted for use with any of the impregnating techniques described. The vapor application method does, of course, require special equipment.

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In its simplest form the equipment required for hot or cold roller coating is shown in the diagram Fig. 1 on page four.

Machines are manufactured specifically for the application of diphenyl formulations to tissue and can be obtained complete with four-color printing and sheeting equipment.

Estimation of Diphenyl

Although weight increase of the treated paper represents a rough guide to the rate at which the diphenyl is being applied, factors such as volatilization of the preservative during processing and the possibility of diphenyl separating from the coating formulation before impregnation, often necessitates the periodical employment of a more specific method of estimation as a check on the weight increase figures.

1. Determination of diphenyl in impregnated fruit wrapping paper

A total of about 200 sq. in. paper is measured out and weighed. This sample of paper is then folded and cut into suitably sized pieces, care being taken to handle the paper as little as possible.

The sample is extracted with cyclohexane for five hours.

Provided the amount of diphenyl being determined is large enough, the extract is evaporated down until a concentration of diphenyl of the order 0.7-1.2% is obtained, this being the optimum concentration for analysis. If the amount of diphenyl to be expected is low, the extract can be evaporated down to 0.2 ml., if necessary. (The lowest concentration which can be measured is 0.01%.)

The absorbance of the final extract is measured at 13.57 and 14.29 microns in an absorption cell of length 0.2 mm. The instrument used for this purpose is the Grubb Parsons (S4) double beam infra-red spectrometer.

The concentration of diphenyl in the extract is read off the calibration curve prepared for each wave length. Thus, two independent measurements of absorbance are obtained, and as it is most unlikely that interferenoe due to any other components will be the same at each wave length used, any effect of interference can be checked.

The following details summarize the spectroscopic measurement:

Absorption cell length:		0.2 mm.
liquid capacity:		0.1 ml.
Absorbance of 1% solution of diphenyl	at 13.75 microns:	0.615
	at 14.29 microns:	0.465
Spectrometer slit width:		0.1 mm.
Minimum absorbance which can be measured		0.005

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Thus, the accuracy of determination of 0.1 mg. diphenyl in solution in 0.2 ml. of final extract is of the order ± 0.02 mg.

2. Determination of Diphenyl in Citrus Fruit

The diphenyl is removed from the minced peel or pulp by steam distillation, followed by extraction of the distillate with cyclohexane. The procedure followed is then the same as the above.

Some success has also been obtained by direct extraction of the peel with cyclohexane in a Soxhlet extractor.

Packaging of Diphenyl Impregnated Paper

The volatility of diphenyl is such that if a single sheet of impregnated paper is left exposed to the air, virtually all the preservative it contains will have volatilized within twenty-four hours. It is, therefore, of the greatest importance that impregnated paper should be wrapped immediately after processing has been completed.

Kraft paper or glassine are recommended as suitable wrapping materials, but polyethylene film cannot be recommended on account of its having high diphenyl-vapor permeability. The following packaging procedures are suggested.

Reels of Impregnated Tissue-

The free end should be stuck down and the reel wrapped around with kraft or glassine paper. Loss of diphenyl through the ends of the reel is insignificant and these need not, therefore, be protected.

Cut Impregnated Tissue Wrappers -

They should be stacked into convenient sized bundles and then wrapped in kraft or glassine paper. The package should be carefully sealed with adhesive tape.

Impregnated Board Panels -

They should be made up into stacks with the impregnated surface inwards and bound tightly with tape. Alternatively, the stacks may be wrapped in kraft or glassine paper and the whole package bound with tape.

Impregnated Paper Panels -

They should be packaged in the same way as cut tissue wrappers.

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For domestic orange and lemon boxes, generally, each half box is treated with 6 grams diphenyl or 25 pounds biphenyl per ton box board, or 50 pounds of 50-50 diphenyl wax per ton of box board. The usual biphenyl treatment for collars requires approximately four pounds of diphenyl per 1,000 square feet of collar. Of course, eight pounds would be required if one is using 50-50 mixture of diphenyl and wax.

The maximum tolerance limit for diphenyl set by the F.D.A. in the Federal Registrar of July 6, 1956, is 110 ppm in oranges and lemons. Early this year, 1961, the U. S. Food & Drug Administration has now extended the 110 ppm tolerance for diphenyl in oranges, grapefruit, and lemons to all varieties of citrus fruits such as tangerines, tangelos, limes, citrons and kumquats.

The maximum tolerance limit for diphenyl set up by the German Government is 70 ppm. The citrus industry should be very happy that the extension has been granted. A shipper can now ship mixed truck loads of various citrus fruits whereas, in the past, he was only allowed to ship oranges, grapefruit and lemons. As a result, diphenyl sales to the paper and carton manufacturers and to the citrus packers should increase.

For further information on further proof of diphenyl effectiveness for the protection of citrus fruits, analytical methods, F.D.A. requirements and application methods, we would suggest interested parties to contact directly the following institutions for more specific information.

1. The Institute of Paper Chemicals
   Appleton, Wisconsin

2. The Fourdrinier Kraft Board Institute
   99 Park Avenue
   New York, New York

These two institutes have had tremendous experience in this area, and I am sure, they will give freely to any paper company all the information needed, if they are a member of the group.

A word of caution: The methods of application of diphenyl and the proof of the tolerance limit of 110 ppm, must satisfy the F.D.A.

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SOLUBILITY TABLE FOR TECHNICAL DIPHENYL

Type of Solvent	Solvent	Solubility in gm. biphenyl/ 100 cc. Solvent	Temp. °C
Hydrocarbon	Mineral Spirits	16.9	26
	Gasoline (Texaco)	24.1	26
	Kerosene	17.5	27
	Benzene	81.5	27
	Xylene	56.9	27
	Turpentine	24.2	24
	Toluene	62.0	18
Hydroxy Derivative	Methyl Alcohol	7.45	24
	Ethyl Alcohol (3-A)	6.7	28
	n-Butyl Alcohol	9.1	27
	Amyl Alcohol	10.3	22
	Glycerine	Insol.	Rm. Temp.
	90% Phenol	17.8	28
Ethers	Ethyl Ether	57.8	24
	Cellosolve Acetate	50.3	25
Ether Alcohol	Cellosolve	22.5	21
	Carbitol	14.5	27
	Diethylene Glycol	Insol.	Rm. Temp
Ester	Methyl Acetate	48.4	24
	Ethyl Acetate	56.6	22
	Butyl Acetate	73.4	29
	Amyl Acetate	55.4	27
	Ethyl Lactate	25.6	25
	Diethyl Phthalate	30.2	26
	Tricresyl Phosphate	50.0	34
Chloro Derivative	Chloroform	110.0	19
	Carbon Tetrachloride	66.4	22
	Ethylene Dichloride	111.0	23
	Trichloroethylene	95.2	23
	Tetrachloroethane	106.2	22
	Monochlorobenzene	93.2	23
	Orthene	103.0	29
Ketone	Acetone	55.8	19
Aldehyde	40% Formaldehyde	Insol.	Rm. Temp
Amine	Aniline	44.6	22
	Pyridine	40.0	25
Drying Oil	Tung Oil	36.8	34
	Linseed Oil	28.0	26
Acids	Acetic Acid	15.8	26
	Oletic Acid	20.2	25
Miscellaneous	Nitrobenzene	81.4	25
	Carbon Disulfide	149.6	26
	Distilled Water	Insol.	Rm. Temp

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THE TOXICITY OF DIPHENYL

The following data was extracted for toxicity studies by R. G. Tomkins and F. A. Isherwood, Analyst, 1945, 70, 330.

Ingestion of Single Doses

Diphenyl suspended in gum acacia solution or dissolved in nut oil has been given by stomach tube to cats in doses up to 1 g/kg. of body weight without causing any visible ill effect.

Ingestion of Repeated Doses

With many aromatic compounds the effects produced by their repeated administration are quite unlike those produced by a single dose; the blood forming tissues, in particular, are often poisoned by prolonged exposure to concentrations far below those immediately lethal. For this reason it is always necessary to determine the chronic as well as the acute toxicity of any substance which may be administered repeatedly to man. Young rats are suitable test objects for this purpose, since any cumulative effect on the substances might be manifested in a departure from the normal growth rate.

Diphenyl - Sixty male white rats, weighing between 35 and 75 g. were divided into four equal groups of the same mean weight and fed ab libitum on the stock laboratory diet. Each rat was given 0.005 ml. of nut oil per g. of body weight daily by mouth and was weighed every second day. Group 1 received no biphenyl. The oil administered to groups 2, 3 and 4 contained 0.4 and 40 mg/ml respectively of diphenyl; the daily intake of the compound was thus 2, 20, 200 mg/kg for these three groups. There was no significant difference between the mean growth rates of the 4 groups during the four weeks of the test, and no animal showed any sign of ill health attributable to the diphenyl feeding. At the end of the test, the blood of six rats from Group 1, and six rats from Group 4, was examined. Hemoglobin content, total white cell count and differential white cell count were normal in all cases.

Parenteral Administration

Diphenyl - No sign of irritation followed the injection of 0.5 ml of a 4% solution into the skin of a rabbit's ear, or the rubbing of such a solution into the skin of the forearm of two human subjects. The intraperitoneal injection of 0.5 g/kg into a rabbit in the form of an oily solution or acacia-saline suspension had no ill effect.

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Inhalation of Vapor

The vapor pressure of both compounds is, at ordinary temperature, so low that the risk of a toxic quantity entering the body through the lungs seems remote. A mouse kept for six hour periods on two successive days in air saturated with diphenyl vapor at 20°C showed signs of discomfort during the exposure, but appeared normal soon after being removed from the chamber, and showed no sign of injury later.

These experiments emphasize the low toxicity of both compounds, especially of diphenyl, which appears to be pharmacologically nearly inert. The doses given to the animals in these tests were, of course, far greater than would ever be ingested by anyone eating oranges from treated wraps. Thus, supposing that the peel of such oranges contained uniformly 20 mg/100 g of diphenyl (the highest concentration found by Tomkins and Isherwood), and supposing also that the rat and man are equally sensitive to this compound, then a 60-kg man eating the peels of ca. 400 oranges a day would still not be getting enough preservative to do him any harm. The amounts of the substances in orange pulp and in marmalade made from treated oranges are still more negligible. The low toxicity of diphenyl when given by injection or inhalation shows that the handling of treated oranges and wraps is not dangerous to health.

Description and Properties of Diphenyl

Diphenyl; Biphenyl; Phenyl Benzene; $C_6H_5.C_6H_5$ or $C_{12}H_{10}$; The compound is indexed by the American Chemical Society at "Biphenyl" rather than "Diphenyl" to conform to the nomenclature adopted by the Society. The formula is preferably written as $C_6H_5.C_6H_5$ to distinguish it from acenaphthene which has the same molecular formula of $C_{12}H_{10}$.

Molecular weight 154.20. Contains by theory 93.46% carbon and 6.54% hydrogen.

Diphenyl is formed by the linking together of two benzene nuclein, or in effect, a hydrogen atom of benzene is replaced by phenyl.

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Properties of Pure Diphenyl

Molecular Weight	154.20
Boiling point at 760 mm	255°C
Boiling point at 10.5 mm	118
Crystallizing point	69.0°C
Melting point	69°C
Solution point	
Specific gravity at 77/4°C	0.9896
Specific gravity at 20/4°C	1.041
Refractive Index 77.1°C	D-1.58822
Viscosity at 100°C	28.8 Say. Sec.
Viscosity at 70°C	31.2 Say. Sec.
Surface Tension at 129.2°C	39.5 dyne/cm
Solubility in Water	
Solubility in abs. % alc. at 19.5°C	9.98 G. 100 g. sol. Seidell
Solubility in 100% Methanol 19.5°C	6.57 g/100 g. Solvent
Benzene at 27.9°C	137 g/100 g. Solvent
Heptane at 26.5°C	25.1 g/100 g. Solvent
Flash point °F (method	235°F - closed cup 255°F - open cup
Fire point °F	
Heat of combustion Kg-cal. (15)	per gm. mol. - 1504.4
Latent heat of fusion	23.8 gm. ca 1/gm. or 53.1 BTU,
Latent heat of vap. at 69.2°C	90.0 BTU per lb.
Specific heat at 40°C	1.61 joule/gm
Critical temperature	
Critical pressure	
Pounds per gal. at 77°C	8.23 lbs. per gal.

Monsanto Specifications

Appearance: Colorless to pale yellow crystallized solid or flakes

Freezing Point: 68.7°C minimum

Distillation Range: 2.5°C maximum, including 255°C

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