Application of Vegetable Oils and their Oleochemicals in Pesticide Formulations

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INTRODUCTION

Pesticide is an inclusive term for a number of individual chemicals designed specifically for the control of pests. Most of the pesticide names are specific to the pests, for example, insecticides, herbicides, fungicides and bactericides are used for insects, weeds, fungi and bacteria respectively.

The majority of the pesticides are made available to the end users as formulated products, where the active ingredients are prepared in forms which are convenient for their intended uses (Abdul Rani, 1993). In general, an active ingredient may be applied in a dry state, in the form of dusts, powders and granules, or in a liquid state as aqueous concentrates, emulsifiable concentrates, suspension concentrates and wettable powders, or in a gaseous state as fumigants.

In the pesticide industry, the production of pesticides is mainly formulated as aqueous concentrates for herbicides, as emulsifiable concentrates for insecticides and as wettable powders for fungicides. These three formulations

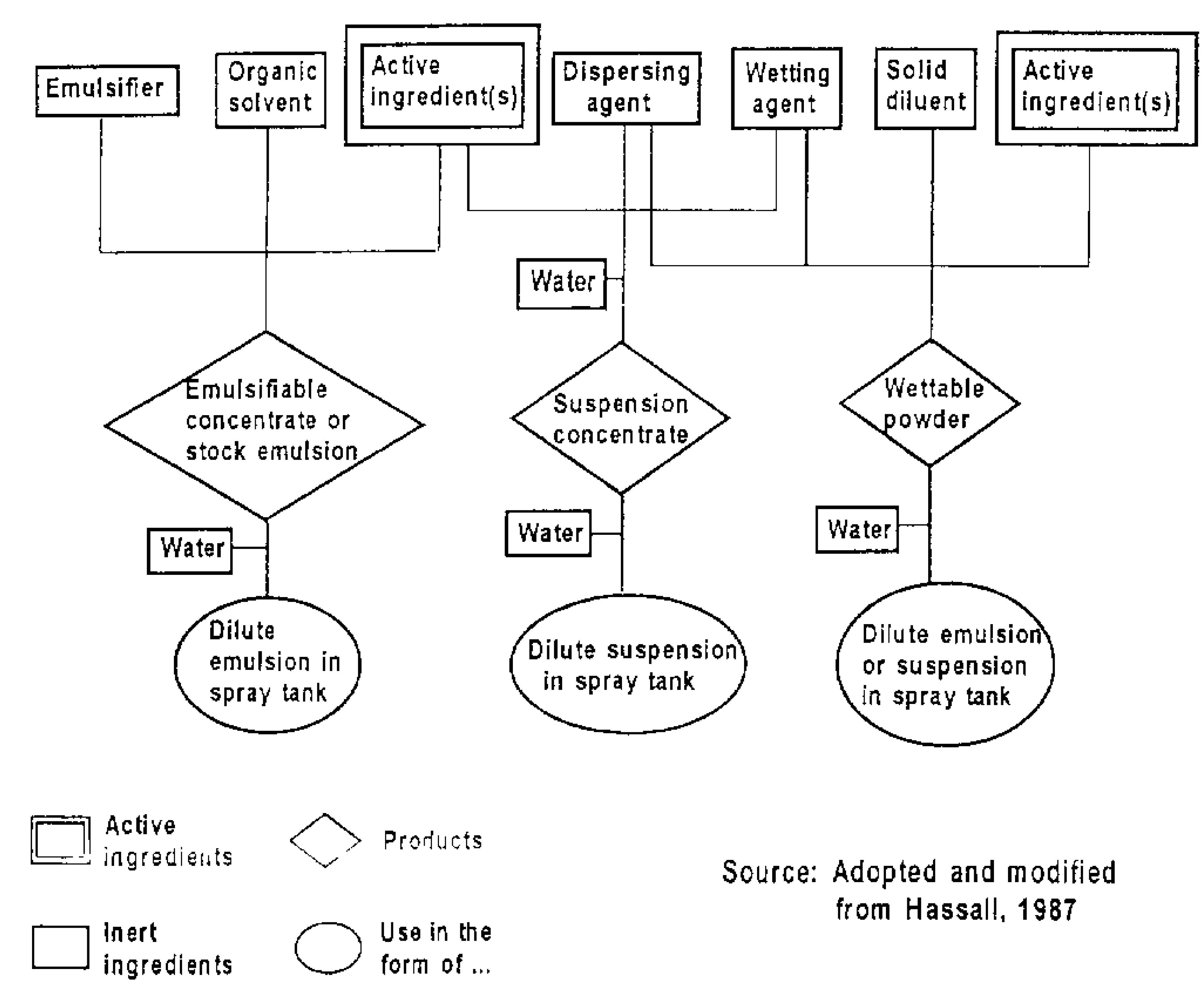

Figure 1. Possible components of spray mixtures.

which accounted for more than 80% of the total pesticide formulations are from liquid state formulations (Seaman, 1990; Pesticide Board Malaysia, 1994).

In general, preparation of pesticide formulations will include two main components, i.e, the active ingredients and inert ingredients. Active ingredients mean the chemical or chemicals in a product responsible for the desired effect, which are capable of preventing, destroying, repelling or mitigating insects, fungi, weeds, rodents, or other pests. Meanwhile, inert ingredients also called supplements, are inactive ingredients which have no pesticidal action (Bohmont, 1990). There are various types of inert ingredients normally found in pesticide formulations, for example, emulsifiers, organic solvents, dispersing agents, wetting agents, *etc,* as shown in *Figure 1.* This paper deals with the applications of vegetable oils and their oleochemicals in pesticide formulations.

VEGETABLE OILS AND THEIR OLEOCHEMICALS IN PESTICIDE FORMULATIONS

Oils and fats, particularly vegetable based are important raw materials for the chemical industry worldwide. *Table 1* shows the world production of oils and fats in 1994 (Mielke, 1995). Palm oil ranks second on the list of oils and fats produced and traded in the world.

TABLE 1. WORLD PRODUCTION OF OILS AND FATS, 1994

Type	Quantity (million tonne)
Soya bean	19.37
Palm	15.34
Rapeseed	10.31
Sunflower	8.23
Groundnut	4.13
Cotton	3.76
Coconut	3.13
Olive	1.82
Palm kernel	2.01
Tallow & greases	7.48

About 90% of palm oil production are used for food products and the remaining 10% for non food products or oleochemicals applications (Salmiah, 1994). Although the latter is smaller in volume, its significance is by no means diminished since most of the palm oil products are further processed to higher value added products. With the expected growth in palm oil production and the general tendency for the industry to go for downstream activities, this area is expected to be of increasing importance. One of the potential uses of these oleochemicals is to replace mineral oils and their derivatives in pesticide formulations.

Vegetable oils and their oleochemicals have major advantages over mineral oils in that they are renewable, readily available all around the world, often as a result of by-products from other industrial activities. Also, they are generally biodegradable, non flammable and cause fewer medical problems and allergies to the end users (Leysen, 1992). Baumann and Biermann (1994) showed that oils and fats are biological raw materials which are constantly renewed. This will be reflected, at least in the long term as an economic advantage for chemical products from oils and fats, compared with those from mineral oil. Favourable ecological characteristics can be expected from linear fatty acid molecules which have no branches or ring structures.

Vegetable oils such as coconut, soyabean, corn, palm and palm kernel oils and their oleochemicals are used to produce inert ingredients like surfactants, wetting agents, dispersing agents, emulsifying agents, adjuvants, solvents, carrier/ diluents, *etc.* for pesticide formulations.

SPRAY ADJUVANTS AND SOLVENTS

The structure and general properties of mineral and vegetable oils used as spray adjuvants had been studied (Hamilton, 1993). *Table 2* shows the fatty acid compositions of some vegetable oils.

TABLE 2. FATTY ACID COMPOSITIONS OF SOME VEGETABLE OILS

Oil	Fatty acid								
	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:1	22:1
Soyabean	–	12.0	–	3.6	23.7	51.4	8.8	–	–
Cottonseed	1.1	27.3	1.4	3.1	16.7	50.4	–	–	–
Linseed	–	6.5	tr[a]	4.5	19.5	16.5	53.0	–	–
Palm	1.0	43.1	0.2	4.0	39.0	10.0	0.2	–	–
Palm Olein	1.0	39.8	tr	4.0	42.8	11.0	0.3	–	–
Peanut	–	9.8	0.4	3.7	60.9	18.1	–	–	–
Sunflower	–	6.0	–	3.0	27.0	64.0	–	–	–
HEAR	–	3.0	–	2.0	22.6	15.0	14.0	15.0	28.0
LEAR	–	4.0	–	2.0	56.0	26.0	10.0	2.0	tr

a = trace   HEAR = high erucic acid rape oil   LEAR = low erucic acid rape oil

Palm oil, which is semi solid in temperate climates, is not suitable to be used as spray adjuvants. However, other vegetable oils including palm olein which is a liquid fraction from palm oil products would be satisfactory.

Leysen (1992) indicated that vegetable oils such as soyabean, cottonseed, linseed, peanut, rape, sunflower, *etc.* adhere better to leaves of plants or insects even after heavy rainfall because of their polyunsaturated nature. This increases the persistency of the active ingredients, making further treatment of the crop unnecessary and hence, allowing considerable cost reductions. Moreover, the quantities of active ingredients lost to the environment are reduced. *Table 3* shows the physical properties of some pure triacylglycerols, fatty acid methyl esters and mineral oils. Hamilton (1993) and recently, Ismail (1995) indicated that methyl esters and hydrocarbons (mineral oils) which have comparable viscosities and surface tensions are suitable vehicles for the transport of pesticides onto the surface of plants or insects.

Kapusta (1985) evaluated the concentrates of soyabean oil (SOC) and petroleum oil (POC) as enhancing agents with postemergence herbicides, such as sethoxydim, fluazifop - butyl and HOE 581 (code name) for Johnson grass control in soyabeans. Results from this study and more recent research (Henkel, 1995) indicated that SOC is equal to POC in enhancing the activity of essentially all postemergence herbicides.

TABLE 3. PHYSICAL PROPERTIES OF SOME PURE TRIACYLGLYCEROLS, FATTY ACID METHYL ESTERS AND MINERAL OILS

Oils	Physical properties		
	Viscosity (mPas)	Surface tension (mNm^{-1})	Boiling points (°C)
Trilaurin	9.11[a]	–	244
Trimyristin	11.70[a]	–	275
Tripalmitin	14.67[a]	–	298
Tristearin	18.50[a]	–	313
Methyl laurate	1.13[a] 3.60[b]	24.3	141
Methyl myristate	1.53[a] 4.10[b]	25.0	156
Methyl palmitate	–	25.7	18
Methyl stearate	2.36[a] 5.85[b]	26.1	215
Solvesso 100*	0.47[a]	29.0	166–179
Solvesso 150*	0.64[a] 2.15[b]	30.0	182-203
Solvesso 200*	1.13	35.9	227-284

[a] at 75°C   [b] at 26°C
* An example of trade name for mineral oils

Henkel (1995) has produced and commercialized various types of methyl esters from vegetable oils, for example, methyl laurate, methyl oleate, methyl soyate, methyl sunflowerate, methyl coconate, *etc.* They are found to be biodegradable, have low toxicity with LD_{50}> 20 g/kg, low viscosity mobile fluids (< 7 cps at 25°C), with good solvency and adjuvant functions.

TABLE 4. PESTICIDE SOLUBILITY (Wt %) AT 25°C (Garst, 1995)

	Solvent		
Pesticide	**E-2209**	**E-2270**	**E-2301**
Malathion	M	M	M
Permethrin	78	67	60
Chlorpyrifos	74	66	60
2, 4 – D isooctyl	M	M	M
esters Dimethoate	12	4.2	2.7

E-2209 = Methyl caprylate/caprate
E-2270 = Methyl laurate
E-2301 = Methyl canolate
M = Miscible in all proportion

Table 4 shows the solubility of various insecticides in methyl esters derived from vegetable oils. The results indicated that methyl esters from vegetable oils have good solvency property to pesticide. The pesticide solubility varied from 3.0 % (w/w) solubility to miscible in all proportion.

SURFACTANTS AND WETTING AGENTS

Surfactants are commonly used in formulations of foliar-applied agro-chemicals to improve physical/chemical properties of the spray solution and to enhance uptake and efficacy of pesticide (Knoche and Bukovac, 1993). Surfactants may increase solubility of the active ingredient in the spray solution. They may also affect spray retention, droplet spreading, and dry rates, and further, recent data suggest that some surfactants may alter cuticular permeability. Enhancement of pesticide uptake by surfactants may be affected by dose and physicochemical properties of the active ingredient and surfactant, and the nature of the plant surface (Gaskin and Holloway, 1992).

The non-ionic surfactants are the most common surfactant used with pesticide. For example, fatty alcohol ethoxylates, the most important class of non-ionic surfactants, are produced by the alkali or acid catalysed reaction of fatty alcohols with ethylene oxide. Because of the current interest in obtaining surfactants largely from natural starting materials for ecological reasons, carbohydrates (starch, sugar, etc) as renewable biological products are gaining more and more importance along with

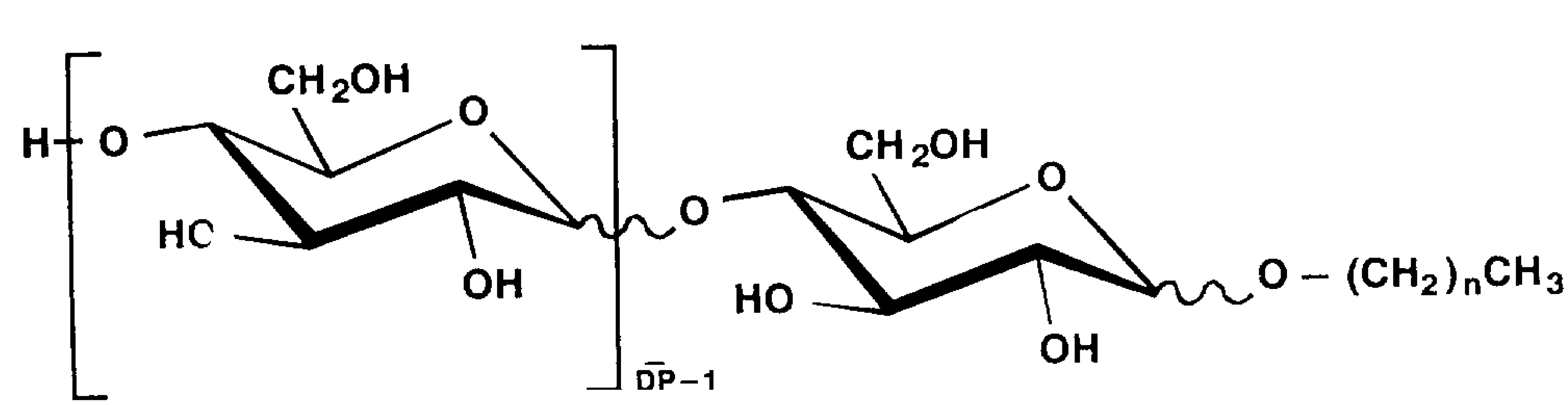

Figure 2. Generalized structure of alkylpolyglycosides (APG).

natural oils and fats for this purpose (Baumann and Biermann, 1994).

Increasing environmental concerns and preference for renewable raw materials generated interest in linking the two groups of such materials – oils and fats, and carbohydrate. Surfactants in which a longer alkyl residue (C8-C22) is rendered hydrophilic by means of carbohydrate instead of ethylene oxide have been the subject of intensive test for decades.

A carbohydrate molecule and the alkyl chain can be linked by means of ester, ether, amide or amine bridges as shown in *Table 5.*

TABLE 5. POSSIBLE TYPES OF LINKAGE BETWEEN CARBOHYDRATE MOLECULES AND ALKYL GROUPS

Carbohydrate - derived surfactants		
Sugar unit	**linkage**	**hydrophobic group**
Sucrose	$- O - \overset{O}{\overset{\|\|}{C}}$	
	- O -	fatty alkyl chain
Glucose	$- NH - \overset{O}{\overset{\|\|}{C}} -$	
Sorbitol	- NH -	

Alkyl polyglycoside (APG), a class of non-ionic surfactants is sugar ethers produced by using glucose derived from corn or potato starch and fatty alcohol from coconut, palm and palm kernel oils (Garst, 1995; Baumann and Biermann, 1994).

The Agricultural Specialities Group of Henkel Corporation (1995) has produced various types of APG to assist the agricultural chemical formulator in developing environmentally friendly agricultural products as shown in *Table 6.*

TABLE 6. TYPES OF ALKYLPOLYGLYCOSIDES AND THEIR CHEMICAL COMPOSITIONS

Alkyl polyglycoside	Alkyl chain	Average DP*
Agrimul PG 2076	8/10 (45:55)	1.5
Agrimul PG 2067	8/10 (45:55)	1.7
Agrimul PG 2069	9/10/11 (20:40:40)	1.6
Agrimul PG 2062	12/14/16 (68:26:6)	1.4
Agrimul PG 2065	12/14/16 (68:26:6)	1.6
Agrimul PG 2072	8/10/12/14/16 (30:37:22:9:2)	1.6

* = Degree of Polymerization

APG exhibits excellent wetting and surface tension/interfacial tension reduction properties, outstanding hydrotropic and dispersant properties as well as superior electrolyte and hard water tolerance compared to the existing surfactants from petroleum – based materials.

This study conducted by Henkel (1995) had compared the wetting performance of Agrimul PG 2067 and 2069 with polyoxyethylene (9.5) nonylphenol, a typical component of many commercial surfactants. It was apparent that spreading and wetting properties of these materials were comparable.

CONCLUSION

The oleochemicals have major advantages over mineral oils in that they are renewable, readily available all around the world, environmental friendly, non flammable and cause fewer medical problems and allergies to the end users.

At present, extensive research is being conducted to determine the application of vegetable oils and their oleochemicals in pesticide formulations. The results indicated that vegetable oils and their oleochemical products have

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major advantages over products obtained from petroleum oils. Therefore, oleochemical products from palm and palm kernel oils too have the potential to be used as inert ingredients for pesticide formulations in Malaysia. ■

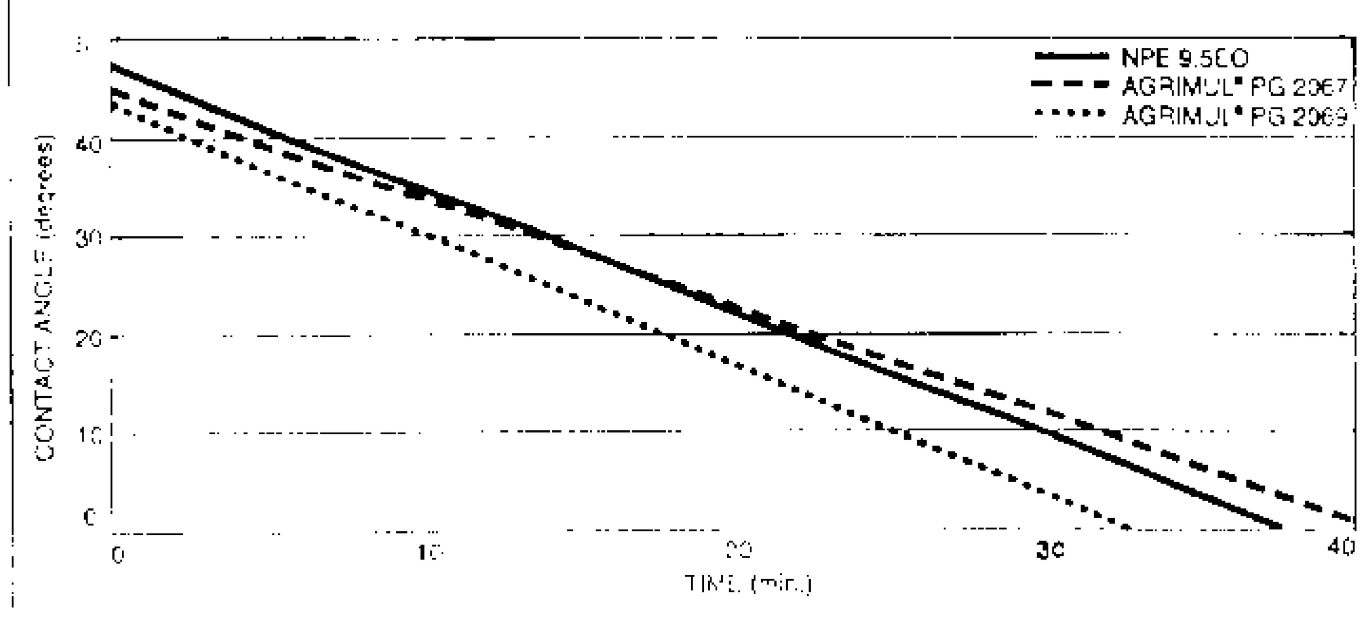
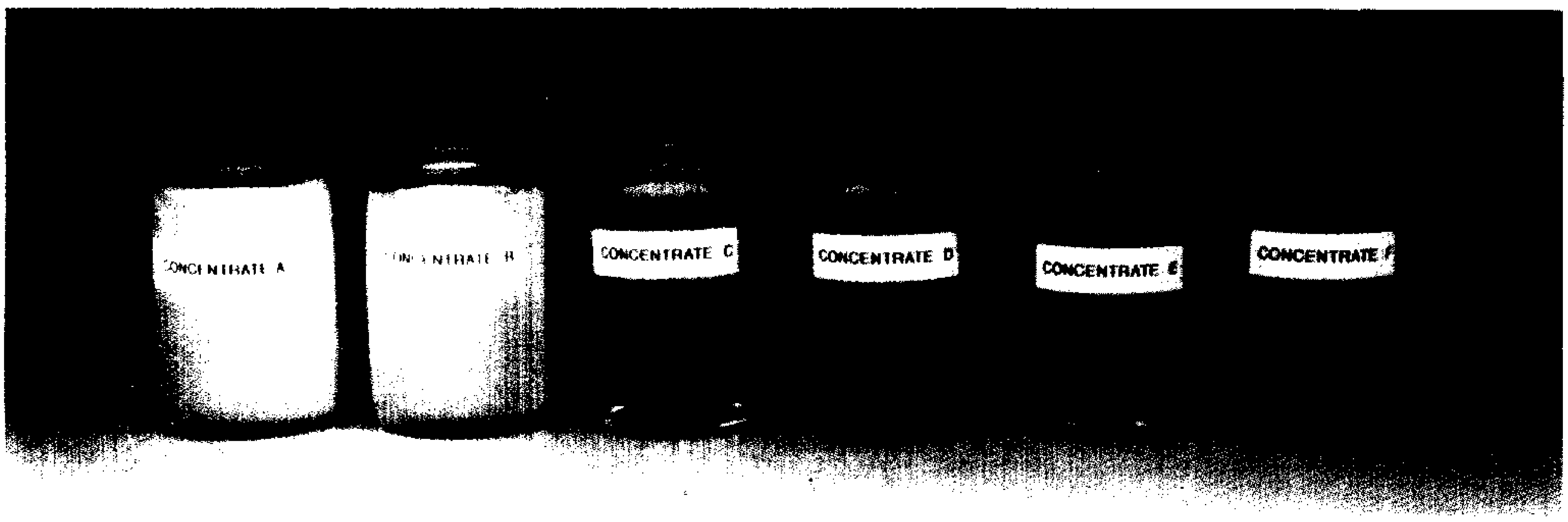


Figure 3. Wetting/penetrating study – Paraffin substrate.



REFERENCES

ABDUL RANI, A (1993). Pesticide formulations - Present trends and recent development. *The Planter, 69* (802): 3–13.

BOHMONT, B L (1990). Glossary for pesticide users . *The Standard Pesticide User's Guide.* Revised and Enlarged. Prentice Hall, Inc: 367 & 392.

BAUMANN, H and BIERMANN, M (1994). Oleochemical surfactants today. *ELAEIS. The International Journal of Oil Palm Research and Development. Vol 6 (1):* 49–64.

GARST, R (1995). Alkyl polyglycosides. *Paper presented in Natural Oleochemicals as Adjuvant in Agro-Chemical Formulations.* Organised by Henkel Oleochemical (M) Sdn. Bhd., 9 October 1995, Kuala Lumpur.

GARST, R (1995). Methyl esters. *Paper presented in Natural Oleochemicals as Adjuvant in Agro-Chemical Formulations.* Organised by Henkel Oleochemical (M) Sdn. Bhd., 9 October, 1995.

GASKIN, R E and HOLLOWAY, P J (1992). Some physicochemical factors influencing foliar uptake enhancement of glyphosate-mono(isopropylammonium) by polyoxyethylene surfactants. *Pestic. Sci. 34* : 195–206.

HAMILTON, R J (1993). Structure and general properties of mineral and vegetable oils used as spray adjuvants. *Pestic. Sci. 37*: 141–146.

HASSALL, K A (1987). Physicochemical aspects of pesticide formulation and application. *The Chemistry of Pesticides: Their Metabolism, Mode of Action and Uses in Crop Protection:* 22–45.

HENKEL (1995). Agricultural solutions. *A Newsletter for the Agricultural Industry.* Henkel Corporation, 11501 Northlake Drive, Cincinnati, OHIO.

ISMAIL, A R (1995). Viscosity of methyl esters. Project CT 289/95, *PORIM*.

KAPUSTA, G (1985). Uses of soybean oil in the application of herbicides. *J. of American Oil Chem. Soc., 62(95)*: 923–926.

KNOCHE, M and BUKOVAC, M J (1993). Interaction of surfactant and leaf surface in glyphosate absorption. *Weed Science. 41*: 87–93.

LEYSEN, R (1992). Non-edible applications of soybean oil. *Lipid Technology. 4(1-6)*: 65–69.

MIELKE, T (1995). Oils and fats : World summary balance (million tonnes). *Oil World Annual 1995*: Summary 7 – Summary 9.

Pesticide Board Malaysia (1994). Pesticide formulations registered in Malaysia. In Registered Pesticide 1992–1994.

SALMIAH, A (1994). Palm Based Oleochemicals and their uses. *Selected Readings on Palm Oil and Its Uses. PORIM*: 160–182.

SEAMAN, D (1990). Trends in the formulation of pesticides. *Pestic. Sci. , 29:* 437–479.