



Relative Volatilities of Dylox^R
Solutions in Methyl Cellosolve and
Tetrahydrofurfuryl Alcohol

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Dylox[®] for ULV spraying has been supplied as a concentrate containing four pounds per US gallon in Tetrahydrofurfuryl alcohol (THFA). Chemagro also supplies liquid Solution F (LSF) containing 4 lb/gal in methyl cellosolve (MC) - a much cheaper solvent. In discussions with Drs. Ken Howard (Chemagro) and J.A. Armstrong (CCRI) questions were raised concerning the possible effects of the high volatility of the solvent on deposit efficiency and effectiveness when LSF is used as a substitute for the earlier ULV formulation.

First, a look at the vapour pressure curves for these solvents. Methyl cellosolve (ethylene glycol monomethyl ether) also sold as Dowanol EM, has a vapour pressure curve nearly identical to that of octane, which should classify it as a dangerous solvent. That of THFA is close to that of undecane (C₁₁) and comparable to those of the more volatile components of #2 fuel oil, which is an operationally acceptable spray diluent. The flash and boil points and vapour pressures @ 20°C for these two solvents are compared with those of water and tripropylene glycol methyl ether (Dowanol TPM) in the following table:-

	Vap. Press. 20°C mm Hg	Boil Pt. °C	Flash Pt. °C
TPM	.03	242	121
THFA	.55	180±	80±
MC	8	124.6	49
Water	175	100	-

TPM has been found to be a satisfactory solvent-diluent for forest ULV spraying in experimental studies conducted by CCRI.

To examine the potential evaporation from sprays of the two formulations, samples of each were dyed with \approx .5% Rhodamine B liquid and run through our stain-drop ratio calibration procedure. The fluid is fed via a multi-ratio gearmotor-driven displacement syringe onto a rotary drop generating device, and formed into drops of which the initial volumes are approximately equal and a function of volume emission and rotor speed (one drop per revolution). Samples of the emitted drops are impinged on Kromekote [®] cards and the matured stains measured and related to the nominal drop diameters. The relationship for low vapour pressure fluids usually takes the curvilinear form:

$$X = a y^m$$

where X is drop diam, Y is stain diam, m is a power, usually between .7 and 1.0 and a is the proportionality constant. This is transformable to the rectilinear form

$$\log X = \log a + m \log Y$$

or when the untransformed data are plotted on log log coordinates, they describe a straight line of slope m and log scale intercept value a. These parameters can be approximated by inspection or the least squares fit line obtained by log linear regression analysis.

However, in the case of more volatile solvents, there may be appreciable evaporation from the fluid surface on the feed head and rotor tip, during drop generation and fall. The deposited drop, of lowered residual volume will make a smaller stain than its unevaporated counterpart. When the points are plotted against the log linear regression line they usually deviate curvilinearly, to the left in the middle and right at the ends. The

curve form can be approximated by adjusting m and a and adding a constant 'evaporation' term, such that:-

$$X = a Y^{(m + \Delta m)} + E$$

The size of the evaporation term and its balancing Δm and reduced a constitute a measure of the potential for evaporation from the falling drops. Other things being equal, the slope of the log linear line or the power m may also constitute an evaporation potential index.

The data for Dylox ULV in THFA @ 24⁰ yielded the equation:-

$$X = .802 Y^{.839}$$

with log linear regression coefficient (LR) .9992, but plotted curvilinearly about the line. Trial and error adjustment of the parameters trended toward $m = 1$, ie rectilinear form. Linear regression analysis yielded

$$X = .238 Y + 26.3 \quad \text{LR } .99996$$

The behaviour of the LSF formulation was markedly different. The large drops made irregular stains larger than their THFA counterparts. However, stain size decreased sharply with decrease in nominal drop size, and evaporation of solvent from the generator feed head was such that drops of about 158 μm could not be produced consistently (no trouble at 100 μm with the THFA solution) at ambient temperature 27⁰C. Bathing the generator in the H₂O mist output of a nebulizer resulted in improved performance, probably related to the reduction of local air temperature to ca. 19⁰. Following the linear regression model used in the THFA analysis, the data yielded:

$$X = .139 Y + 120$$

The slope of the log log line at 27⁰ was about .51 and perhaps .58 at 19⁰, vs about .84 for the THFA solution at 24⁰. Obviously the LSF solution is very volatile.

The stains produced by both fluids are strongly fluorescent, especially when fresh, appearing bright orange red when illuminated with green light. However, some stains made by drops of LSF originally near 150 μm in diameter were only weakly fluorescent, appearing darker, and rather magenta in colour like those produced by water solutions of the dye. It is postulated that evaporative cooling may have induced water condensation and resulted in water type stains from drops that had lost most of their original solvent content. In each case there was solid crystalline residue present in the drop trace.

Whereas the THFA solution seems relatively satisfactory for forest ULV spraying, the MC (LSF) solution would seem to be much too volatile, besides being operationally dangerous. Substitution in whole or in part of a heavier glycol ether, ie TPM, or other low volatile solvent, or dilution with same at spray time would be desirable.

The question of the effect of evaporation on spray deposition should be examined. If the downward extrapolation of the linear equation is real, the evaporation term should approximate the size of the drop below which the residual liquid content would be too low to mark the paper on impingement. Under net evaporative conditions equivalent to those existing during the calibration run, the equivalent spray drop might not be wet enough to adhere to the insect or its substrate. Laser holographic methods, such as used by Roberts et. al. (J. Econ. Ent. 64(2): 533-536) could be used to observe and compare the deposition of sprays of Dylox in various solvents and diluents. The necessary equipment and expertise should be available at the Ontario Research Foundation.