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SOLVENTS AND DILUENTS FOR SPRUCE BUDWORM SPRAY FORMULATIONS:

THE PROBLEM OF VISCOSITY & VOLATILITY vs. ATOMIZATION & DEPOSITION

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SOLVENT AND DILUENTS FOR SPRUCE BUDWORM SPRAY FORMULATIONS

THE PROBLEM OF VISCOSITY & VOLATILITY
VS
ATOMIZATION & DEPOSITION

Recent developments which have necessitated replacement of time honoured solvents and diluents in SBW air-spray formulations have forced us to look harder at the problem. The main problem has not changed: how to disperse a toxicant efficiently and in such a manner that it will efficiently penetrate the multitudinous microhabitats and kill the insects in them. "Slip 'twixt cup and lip" is inevitable, as the path is long and fraught with variables--some interdependent. Let us look at the situation in terms of large scale aerial ULV application via multi-engined aircraft as in the Quebec spray operations in recent years.

The spray aircraft with it's emission equipment constitutes a high speed large scale two-fluid external mix pneumatic atomizer which, instead of being a static device with high velocity air going through it, moves through the air at high velocity. It can be thought of as a big multi-jet carburetor throat opened out flat--the nozzles on the boom corresponding to the fuel jets. The behaviour of the fluid emitted from the 'nozzle' is a function of relative air-velocity, fluid surface tension and viscosity (temperature affects viscosity and density), effective air to liquid volume ratio, and nozzle configuration and orientation.

At velocities in excess of ca 50 meters/sec. (200 mph is well above this), atomization is by friction ablation of the fluid surface, unless some of the emitted mass is decelerated to below 50 m/sec. relative velocity in which range atomization is in the ligament and sheet break-up regime, resulting in larger drops. This happens if emission rate is too high.

As surface tension of most oil sprays usually varies over only a narrow range, viscosity of the fluid is the next important factor--high viscosity leads to coarse atomization and low viscosity to fine. Look at gasoline in a carburetor throat--a fine fog, if it is working efficiently.

Nozzle configuration is of less concern than at lower velocities--the open Spraying Systems nozzle bodies in use, oriented only slightly into the airstream appear to work quite well (except with high viscosity fluids) as long as they are not 'overfed' i. e. the effective air to liquid ratio is in the optimum range. This is not to say that the configuration could not be improved to increase the area of fluid surface exposed to the air blast and thus increase the permissible flow rate per nozzle. (See Appendix I)

Having had a quick look at the 'cup' and its pouring spout, let us now look at the 'lip'--the biological target! (See U.K.Solang 1977 re 'biological target'). Several authors have indicated that drops below 40 - 50 µm in diameter are more efficient in penetrating tree canopies and contaminating microhabitats, and those 10 - 20 µm in contacting sheltered larvae. Larger drops, particularly those larger than 100 µm are mostly screened out by peripheral and windward foliage. (This may not be a disadvantage when spraying open feeders like sawflies and forest tent caterpillar).

Actually, only a very small volume of spray can do the job if it contains enough toxicant. (See Appendix II). The alternative is flooding with low concentrate spray as in hydraulic spraying which is out of the question via airspray! Some advocate spraying an intermediate volume of formulation with toxicant concentration lower than ULV rates. This has merit in that with conventional airspray at lower air speeds it may increase uniformity of coverage and the number of fines available for effective deposit, but has an economic disadvantage.

Let us accept for the moment that it is this small end of the drop spectrum that is desirable and that the large end should be held to a minimum for environmental protection and cost efficiency, and that we will be operating with the large high speed aircraft. Accordingly, we must design our system to produce a suitable spray cloud and steer it to the biological targets where as much as possible of it will be of optimum size and toxicant concentration to do the job.

It is this steering bit that constitutes the slip between the cup and the lip. Whereas the larger drops usually settle out and result in measurable deposit levels on flat spray sampling cards, the fines are completely at the mercy of the local meteorology. Accordingly, the range of acceptable spray weather conditions is rather narrow and conditions are seldom ideal. It is not surprising that there have been some 'failures' in operational sprays along with some excellent deposit records on monitored areas, where good recoveries of very small drops, which have notoriously poor deposition efficiency on flat sampling surfaces, were obtained. In some cases good kills have been noted where little or no deposit was recorded on the flat sample cards—presumably drifting fines in the effective range but too much air motion to allow any to settle out onto the cards. An example of an attempt to utilize ideal conditions is represented by spray studies in Western U.S.A. wherein very fine sprays were emitted along the flank of a ridge and natural air drainage down the slope drifted the spray through the tree crowns. Studies on meteorology vs spray deposit efficiency are well in hand in the Institute and sound recommendations re acceptable spray weather should be available.

However, another factor which has so far been only qualitatively recognized is the volatility of the various components of the spray formulations. Loss of volatiles reduces the size of drops in flight thus affecting their trajectories. Thus volatility becomes a factor in the 'steering' part of the problem. It also affects things at the target end of the system. Some fines may be reduced to the extent that they may not reach the target and are thus removed from the 'effective' part of the drop size spectrum. On the other hand, some large drops may be pushed into a more effective range. The deposition picture of the top end of the spectrum will be the least affected. The net effect may be good or bad, depending on the percentage of formulation volume represented by volatiles and their vapour pressure ranges, and the original drop size spectrum produced at the other end of the system where, all things being equal, fluid viscosity is the governing factor.

Thus we have three V's, velocity, viscosity and volatility, all controllable. Our task is to decide what combination of the three will produce the best results under what meteorological constraints. Of the three, the first, airspeed, is independent and the preferred value of the second is somewhat dependent on it. The second and third are somewhat interdependent in that the lower the viscosity of a fluid generally the greater is it's volatility. In addition both factors are strongly temperature influenced so that the spray formulation should be 'tailored' to operating temperature as well as for airspeed and emission equipment and flow rate.

The importance of viscosity has been recognized by Randall who was responsible for the introduction of the No. 2/4 fuel oil mix as a base for airspray formulations. He insisted that the 'light' fractions, #2 oil plus Arotex 3470, and the 'heavy' fractions, #4 oil plus liquid toxicant be balanced 50/50. This rule of thumb usually worked well except for a notable exception. A 1977 spray, incorporating Matacil in viscous nonylphenol solvent with #2/4 mix, gave a poor deposit record--large drops only, and very poor control. In retrospect Randall suggested that the viscosity of the mix was too high at operational temperature (although it may have seemed O.K. under lab conditions). Recently, Hopewell has compared a sample of the mix with formulations, patterned after successful 1977 sprays, which had viscosities in the range 15 - 20 Centistokes in the temperature range 0° to 5° C. It rated at about 50 Cst. This explains the failure and has alerted us to the very real importance of this factor. It was an expensive lesson!

Now we enter a new phase, precipitated by the Exxon #2 fuel oil carcinogenicity report. This has really thrown the wooden shoe among the cogs! Environmental pressures and political expediency having dictated abandonment of our time honoured solvents and diluents, we are now faced with finding suitable replacements. So far, environmentally and economically acceptable substitutes that have been suggested are both less viscous and considerably more volatile than #2 oil. They consist of much the same low boiling point components, but without the low vapour pressure components to give the drops high residual volumes, the cut-off boiling end point being below 600° F. They also require a large proportion of substitute co-solvent (vice Arotex 3470). We had recommended Dowanol TPM as being relatively satisfactory from solvency, cold stability, viscosity and volatility standpoints. As TPM is rather expensive, other solvents have been proposed. Shell Oil is suggesting the use of Cyclo-solv 63 which is more or less comparable for solvency and stability of fenitrothion but which is very volatile and results in a very low viscosity formulation. Sumitomo is also working on this problem.

It is not safe to recommend a fluid with physical characteristics so different from those of formulations which have proved satisfactory in the past--at least until these two factors have been properly evaluated and the optimum spray output spectrum has been determined. An alternative to piecemeal substitution of solvent and diluent, a single base fluid with adequate solvency and correct physical characteristics would be logical and operationally convenient. (See Appendix III). It is obvious that the problem is not simple and needs to be tackled from both ends and the middle as well!

The first requirement is to decide what constitutes an operationally attainable approximation of an optimum spray cloud in the target area. Very little information can be gleaned from past experimental or operational spray programs largely because of inadequacy of the spray deposit sampling system and the rather distant association of the samples with the ultimate biological observation units--individual larvae in their microhabitats. An unequivocal answer would require a full scale intensive study with appropriate resource expenditure. Expertise available in the spray meteorology section could be called upon re specialized spray sampling instrumentation. The question of minimum effective dose of active ingredient in terms of contacting drop size and percentage insecticide content should be resolved. (See Appendix II). Spray dispersal is an engineering problem (Appendix I) which needs input from fluid mechanics and spray physics, particularly in terms of preferred viscosity and the effects of volatility. See Appendix III for discussion of these factors. Another complication lies in the lack of a ready method for tracing and sizing particles which reach the biological target!

The foregoing is a 'worm's eye view' of part of the SBW problem from one vantage point within the system. It is expressed in the hope that it will elicit constructive thought from others, and to point out the importance of tailoring spray formulations to the job in hand.

APPENDIX I

Atomization, Nozzle Configuration and Testing.

When the physicist looks at the open-nozzle delivery system of the TBM, DC-6 etc. spray planes, he looks at it in the simplest possible form: as a clean jet of fluid ejected at a given angle into a rapidly moving air stream. The breakup of such jets has been studied and related to air speed and fluid viscosity, surface tension and other factors. Accordingly, he can predict the behaviour of a fluid in this ideal system and indicate atomization parameters to be expected.

However, the Spraying Systems T-Jet nozzle body (no discs or cap) does not necessarily deliver an ideal jet. The 3/16" orifice is deep in the throat of a cylindrical (strainer) chamber which is conical at the bottom. The combination of Coanda effect (dribbling teapot spout effect) and the buffeting and pressure of the impinging airstream causes the fluid jet to adhere to the sides of the chamber and emerge more or less irregularly onto the upper surface of the body and into the airstream. Ablation of the surface of the relatively immobile fluid by the high velocity air provides atomization into drops in our presumed interest range. The size of drops produced will be a function of fluid viscosity and surface tension principally. Overfeed will result in some liquid being thrown or blown clear and subject to a coarser breakup regime. On this basis it would seem that efficient operation would depend on balancing fluid flow rate against the area of the "nozzle" presenting fluid to the airstream. This is equivalent to optimum air to liquid ratio in conventional pneumatic atomizing nozzles.

More or less on this premise, Randall suggested increasing the periphery of the open end of the "nozzle". Accordingly, I machined a batch of internally tapered adapters which were soldered onto standard nozzle caps which could be screwed onto the 'open nozzle' bodies. These provided the increased terminal periphery and were to have been tested on a TBM aircraft but apparently this could not be arranged. This system would still be subject to the tendency of fluid to adhere to one side of the orifice. This can be overcome by inserting the largest available sizes of orifice and swirl plates to induce hollow cone flow which would impinge evenly on the inner surface of the adapter and thus be distributed uniformly around the increased periphery. This was tried in a laboratory spray fluid flowability testing system and worked as expected. Flanged extension of the terminal surface to 'hold' more fluid for efficient ablation should be examined. NAE (Al Drummond, Pers. comm.) has been examining this 'surface holding' principle in developing an experimental airspray unit.

As there seems to be no experimental wind tunnel, with the necessary velocity and in which the use of oil or toxic sprays is permissible available here, other test arrangements would be necessary. Individual nozzles could be tested in the throat of a large mist blower with adequate air velocity. Assuming that a suitable system for sampling and measuring the output size spectra of the spray clouds can be assembled and operated,* it should be possible to determine ideal fluid viscosity, best nozzle

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* See Reichard, D. L. et al. J. Econ. Ent 71(1): 53-57 for use of "Optical Array Spectrometer Probe" for spray drop spectra measurement.

configuration and optimum flow rate per nozzle. This latter will govern the number of nozzles needed in relation to volume application rate and nominal swath width. Within reason this should be extendable to operational conditions, although calibration flight trials would be desirable.

The foregoing could constitute a separate study within the program and would require considerable resources.

APPENDIX II

Dosage at the Biological Target

Laboratory 'toxicology' studies of insecticides vs SBW in the Institute have been largely a matter of comparing the relative responses of reared larvae to various dosages of active ingredient of various insecticides applied in a range of concentrations in a constant volume of standard fluid to anesthetized larvae. As the fluid application rate was rather high (i.e. ½ gpa) the toxicant concentrations required to bracket the threshold to LD 95 response levels are quite low, compared to field ULV levels. This high volume and the fine atomization attained in the spray tower result in very high particles per unit area deposit levels--in the order of 1000/cm^2 or more. We have no information on the relative effects of the same AI dosages applied at much higher concentrations and at much lower particle densities. This would be desirable for extension to the prediction of effective deposits at the target, of desirable spray cloud characteristics at that level, and backward through the system to the lowest permissible toxicant concentration in the spray formulation.

Laboratory studies in this range are difficult because of the difficulties in producing a desired narrow range of very small drop sizes at very low output rates, and repetitive precise emission of sub-microlitre volumes of fluid through the nozzle. Also, at high AI concentrations, a sub-lethal dose may consist of but a drop or two. Dosage intercepted by individual test larvae will vary widely so that test response is likely to be quite variable.

APPENDIX III

Viscosity and Volatility

The matter of replacement of spray formulation components vice #2 and #4 fuel oils and Arotex 3470 solvent has been under advisement by the Institute and the Houghton committee and ad hoc recommendations have been made re piecemeal substitution. As discussed briefly in the main body of this synthesis, these recommendations have been made without regard for the possible effects of viscosity of the final mixture. Because of the constraints imposed by concern over possible carcinogenicity of components with boiling points above 600° F, proposed substitutes necessarily have a lower boiling point range and, lacking aromatic content, have lower inherent solvency for fenitrothion, thus requiring more co-solvent. Our experience with suitable available industrial solvents has been limited to a glycol ether (Dowanol TPM) which we recommended as a reasonable candidate, even though it is relatively expensive. Chemagro (Ken Howard et. al.) have been consulting independently with Shell Oil (Perry) on this matter. They have suggested a much more volatile and much less viscous cycloparaffin product.

Hopewell is currently evaluating the solvencies and proportions necessary for cold stability, and the viscosities of the resulting mixes of candidate solvents and diluents which seem to fall within the limits imposed by said constraints. Candidate fluids are being solicited from the petroleum companies and other sources. All so far tested have resulted in alarmingly low viscosity values.

The size of drops produced, or the value of a given atomization parameter, is said to be proportional to the ¼ power of the viscosity, other things being equal (Drummond, pers. comm.). This does not seem like much and I question it's applicability to the deposit spectrum at drift distance length from the point of emission, especially with a volatile formulation. The difficulty lies in the fact that concomittant with lower viscosity goes higher volatility. Some evaporative volume loss is usually permissible and may even be desirable. However, if low viscosity leads to finer atomization and the production of fines near the lower limit of acceptability, evaporative loss can so reduce their size that they may no longer reach the target and may constitute a respiration hazard elsewhere! Also, finer atomization results in a greater surface to volume ratio of the spray, thus raising the rate of evaporative loss, and causing the spray drops to remain airborne longer and therefore more subject to the vagaries of the local meteorology.

Looking at the fundamentals, drop diameter varies as the cube root of the volume. Accordingly, if we take an extreme case of a formulation consisting of 10% essentially involatile AI in a readily volatile fluid, the small drops, particularly, will be reduced quickly to a residual volume of less than 12½%, approaching 10%. The corresponding residual diameters would be less than ½ of their original values. 50% volume loss would result in ca 80% residual diameters which should have an appreciable effect, and some of the substitute formulations proposed may well fit into that class when we consider that some of the spray may be airborne for an hour or more. Low operating temperature can be a mitigating factor.

The evaporative behaviour of a simple fluid with a definite vapour pressure/temperature relationship is readily predictable. However, the petroleum products used in spray formulations have wide boiling point ranges, and when two or more from different sources are combined, with additional solute, the evaporation picture is much more complicated and it is difficult to predict the behaviour of a given fraction of the emitted spray. However, techniques exist for observing and measuring the evaporation of individual drops of spray fluids. Hopewell has published an evaporation study of formulations of DDT in a moderately volatile oil and in a low volatile oil. I have in hand a nearly finalized manuscript on the use of teflon coated slides in comparing the relative evaporation rates of several spray fluids. The methods could prove useful where the behaviour is not readily predictable because of a complicated vapour pressure picture.

The piecemeal approach does not seem too promising. Hopefully a less volatile and more viscous diluent with adequate solvency for fenitrothion and other pesticides and environmentally acceptable can be found. A single fluid dispersant, if priced within reason, should be operationally attractive!