

A COMPARISON OF EMPIRICAL EQUATIONS USED TO
APPROXIMATE THE DROP/STAIN DIAMETER RELATIONSHIP
OF A VOLATILE OIL-BASED SPRAY FLUID ON KROMEKOTE[®] PAPER

by

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Report No. FPM-X-8

July, 1978

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ABSTRACT

Empirical equations to describe the drop size to stain size relationship of spray drops on Kromekote[®] paper are derived for eight models, linear, exponential and polynomial, using data from calibrations of four similar oil-based forest spray formulations. Their goodness of fit to the data and their upward and downward extrapolations are compared. Three exponential models include an adjusting term to compensate for evaporative shrinkage of the drops. One seems to provide a good estimate of the relationship to be expected in the absence of evaporative shrinkage. Based on this a model is developed to express the relationship obtaining for the smaller drops where the diameter shrinkage can be no greater than that permitted by a short term evaporated residual volume fraction limit. The use of polynomial models is questioned. Within limits the simple exponential model is adequate for volume deposit measurement but not for drop size spectrum analysis for this moderately volatile formulation.

RÉSUMÉ

À l'aide de données de l'étalonnage de quatre préparations huileuses semblables d'insecticides pour la pulvérisation sur les forêts, on obtient des équations empiriques qui décrivent le rapport dimensions des gouttelettes à celles des taches sur papier Kromekote[®] pour huit modèles linéaires, exponentiels, ou polynômiels. Leur fidélité et l'extrapolation vers le haut et vers le bas sont comparées. Trois modèles exponentiels comprennent un terme qui tient compte de la réduction des gouttelettes par l'évaporation. L'un d'eux semble fournir une bonne estimation du rapport à prévoir en l'absence d'évaporation. Il en découle un modèle exprimant le rapport obtenu pour les plus petites gouttelettes, pour lesquelles la diminution du diamètre ne peut excéder celle que permet une limite de la fraction du volume du résidu qui s'évapore à court terme. L'utilisation des polynômes est mise en question. En deçà de certaines limites, le simple modèle exponentiel permet de mesurer le volume des dépôts, mais ne permet pas l'analyse du spectre des dimensions des gouttelettes pour cette préparation insecticide modérément volatile.

INTRODUCTION

Analysis of deposit sample cards of oil-based aerial sprays require prior calibration of the drop/stain diameter relationship so that measured drop traces can be related, through the size and volume of the drops that made them, to their content of active ingredient. This is done by producing drops of known sizes and measuring the diameters of the spots they make when impinged on similar cards. The resulting laboratory determined relationship, strictly speaking, is applicable to the field sample cards only for essentially involatile fluids, or for those for which a predictable compensation can be made for a known content of very volatile solvent or diluent. The majority of formulations used in forest aerial spraying fall into neither class as they usually contain solvents and diluents with appreciable vapour pressures. Accordingly, falling spray drops are subject to volume shrinkage at rates governed by their surface to volume ratios and ambient temperature. A shrunken drop can be expected to make a smaller spot than its unevaporated counterpart.

A convenient tool for producing drops of theoretically known emitted volume and diameter is the rotary blade drop generator (Rayner and Haliburton 1955). Fluid is metered to the feed mechanism by a gearmotor driven positive displacement syringe. The geometry of the feed head is such that a considerable area of fluid is continuously exposed to evaporation so that the delivered drops are 'preshrunk'. These drops are then equivalent to free falling spray drops which have been subjected to the same net evaporative loss before being deposited on the sample card. From nominal emitted diameters and corresponding stain

measurements one can derive a drop/stain diameter relationship which should approach that which would apply under some spray altitude and air temperature combinations giving the same net evaporative effect.

As presently used, the generator produces drops in a logarithmic series of sizes from 100 μm to 317 μm . Above and below this range we have to depend on extrapolation of some model of equation that fits the data, or on another that is logically derivable from it to allow for a predictable limit for evaporative shrinkage. Reasonable accuracy in this downward extrapolation is important in the analysis of deposit samples of ULV drift sprays.

Where cards with laboratory-produced stains are to be used to calibrate an image analysing machine (spot scanner), the sizes of the images 'seen' by the machine, which will differ somewhat from ocular measurements, should be related to values equivalent to the initial diameters of drops which would have produced similar stains after being airborne. For the 'scanner' calibration, drops smaller than 100 μm are needed and can be generated by an air-assisted point emission nozzle (adapted from that of Buckholtz and McPhail 1960). However, as the liquid feed retention time is very short, the droplets produced do not evaporate as much as their rotary-produced counterparts would. Here one must depend on drop diameters estimated from ocular measures of stain diameter entered into the best available downward extrapolation from the data.

In this study, several models for empirical equations, linear, exponential and polynomial are compared using data from a series of calibrations of field spray fluids.

MODELS

The relationship between the size of an oil drop and its stain on Kromekote paper has been said to be typically described by a polynomial equation of the form:-

$$y = a + bx + cx^2$$

in which y is drop diameter and x is stain diameter (Dumbauld and Rafferty 1977). The special case in which a and c have zero values (i.e. $y = bx$) applies to the uniform spread ratios of non-volatile drops which assume lenticular form when deposited on a perfectly smooth non-absorbent surface. A second case where c equals zero (i.e. $y = a + bx$)* applies to many dyed water-based sprays on absorbent surfaces. Use of the full polynomial requires estimation of parameters a , b , and c appropriate for fitting such a curve to the data. This is mathematically difficult (tedious) unless one has access to a suitable computer program. A more simple model may be adequate.

The stain/drop diameter relationship of unevaporated or involatile droplets of oily fluids deposited on Kromekote paper can be well described by exponential equations of the form:-

$$y = bx^n$$

where x is stain diameter, y is the drop diameter, and b and n are parameters peculiar to both the fluid and the particular lot of paper used. The log log plot of such an exponential curve is a straight line. However, most oil-based aerial spray formulations contain some surprisingly volatile

* Note that this is a special case of $y = a + bx^n$, where $n = 1$, which model will be considered later in this section.

components whose loss during free-fall results in reduced stain size and altered spreading behaviour on the sampling surface.

Plots of drop over stain diameter calibration data of such fluids on log coordinates are usually somewhat curvilinear. The degree of flexure seems to vary with the volatility of the solvent system and indicates the amount of departure from the basic exponential relationship represented by a straight line. The curvature can be described approximately by adding a constant to the drop diameter (y_e) values, corresponding to a series of stain diameters (x), derived from an appropriate exponential line and plotting them against those stain values. The straight line equation: $\log y_e = \log b + n \log x$ where $y_e = y - a$ is equivalent to the exponential equation:-

$$y_e = bx^n \text{ whence } y = a + bx^n$$

Another approximation can be made by graphically estimating a constant, which when added to the observed stain diameters (x) will give x_e values such that:-

$$\log y = \log b + n \log x_e$$

Substituting $x + k$ for x_e in the exponential form yields:-

$$y = b(x + k)^n$$

The first case amounts to increasing the calculated diameter of a deposited drop by the added constant to estimate the diameter it might have been before any evaporation took place. In the second case the stain diameter is in effect increased by a constant to what it might have been had it been made by the unevaporated original drop. A modification of this concept consists in making the transformation term an inverse function of x ,

which increases the size of the term as the stain size is decreased. Such a model was developed for use with a relatively volatile mix of aminocarb and nonylphenol in a special light petroleum diluent:-

$$y = b(x + k/x^{1/3})^n$$

This model can compensate better for the greater percentage volume loss from the smaller drops with their higher surface to volume ratios and longer air-borne times.

PROCEDURES

It is useful to examine the data graphically. Plot nominal emitted drop diameters against estimated (measured) mean stain diameters accurately on log log paper. It is assumed that several samples of spots of each size have been measured to ensure that short term fluctuations in the size of emitted drops have been averaged out to produce a consistent set of data, rather than a scatter diagram. Examine the plot for apparent curvature. A fine straight line scribed on a strip of transparent plastic is a convenient tool for doing this.

Trial values of parameters a and k can be selected by inspection by trial and error positioning of the scribed line such that when a is subtracted from y the resulting points fall along it; similarly a slightly different line can be selected to fit $x + k$. Selection of K involves trial calculation of tables of $K/x^{1/3}$ values for the measured stain diameters. The value of K which gives points that seem to plot on or about a straight line is then a good estimate of the parameter. The slope of the line, which is equivalent to the power n in the exponential equation $y = bx^n$ can

be estimated from the coordinates of two points read from the straight line fitted by inspection, x , y , and x_2 y_2 thus:-

$$n = \frac{\log y_1 - \log y_2}{\log x_1 - \log x_2}$$

The parameter b is estimated thus:-

$$b = \frac{y_1}{x_1^n}$$

The equation should be tested by verifying that

$$bx_2^n = y_2$$

If there is no apparent 'curvature' or imbalance in the deviations of observed *vs.* expected drop diameters (residuals) and they summate to near zero, the values of b and n are probably reasonable estimates. Examples of this systematic curvature are evident in opposite senses in columns 1 and 2 in Table 1. For the graphically estimated values of a or k estimates of b and n can also be obtained by fitting a least squares regression line to $\log (y-a)$ *vs.* $\log x$ (or $\log y$ *vs.* $\log (x + k)$ or $\log (x + k/x_1^{1/3})$). The program for this procedure is built into some small desk and advanced hand held calculators.* Other estimates of b and n should be derived for adjacent values of a (or k etc.) to see if they yield a better fit to the data (i.e. lower sum of squares of residuals, and/or higher coefficient of determination). If one data point seems to affect the slope, level or shape of the line unduly and it is not convenient to further replicate it, try deleting it and recalculate to see if a much better fit to the remaining data results. How do these models compare with the linear, log linear (exponential) and polynomial forms for calibrating the spread of oil-based spray drops on Kromekote cards?

Data from calibrations of four phosphamidon-in-oil spray

* i.e. Monroe Model 1930 & Texas Instruments SR 51 II.

formulations with the same nominal composition but made up with allegedly equivalent components from different suppliers were pooled and used to derive the parameters for eight equation models (see Table 1). The formulation consisted of phosphamidon (92% AI) 14.86%, Arotex 3470 (a wide boiling range aromatic solvent) 50%, #2 fuel oil 3.8%, #4 fuel oil 31.34%. The calibrations were run on the back or screen face of 8.7 mil Kromekote paper, finished on both sides, from the same lot as that used for monitoring the 1977 forest spray operations in Quebec. Two samples (cards) of stains for each available drop size were measured for each fluid using a Cooke AEI image splitting ocular micrometer @ 16X. Plots of nominal emitted drop size *vs.* estimated mean stain diameter and the graphically estimated parameters indicated considerable systematic variation in spreading behaviour among the four fluid samples as well as marked differences from parallel runs on 7.5 mil Kromekote stock. The data from the six sets of eight cards were pooled for ease in plotting and calculation by deriving mean log equivalent stain diameters for each nominal output drop diameter, assuming random fluctuations in emitted drop size to have been averaged out.

RESULTS

Derived forms of six model equations:-

$$y = a + bx \dots\dots\dots 1$$

$$y = bx^n \dots\dots\dots 2$$

$$y = a + bx^n \dots\dots\dots 3$$

$$y = b(x + k)^n \dots\dots\dots 4$$

$$y = b(x + k/x^{1/3})^n \dots\dots\dots 5$$

$$y = a + bx + cx^2 \dots\dots\dots 6$$

plus two polynomial variants appear in Table II with their coefficients

of determination (R^2) and sums of squares of residuals. Calculated equivalent drop diameter values for stain diameters from 0 to 3000 μm , including the data points are listed in Table I. Deviations of the calculated values from nominal means (residuals) are also listed. The sums of their squares and the R^2 values serve as indices of apparent "goodness of fit" of the data to the curves. The two equations (3 and 4) involving transformation constants (a or k) were derived graphically and arbitrarily calculated to pass their lines through the underlined coordinate points. Log linear regression analyses using the same constants (3a and 4a) appeared to give somewhat better fits (lower sums of squares). Further analyses using slightly smaller constants resulted in more improvement (3a and 4b). The differential adjustment of the stain diameter transformation term by the inverse cube root of x (#5) seems to give a still better fit. (see Table II).

The polynomial model (#6) fits the data points well but the extrapolations, both downward and upward, seem to be out of line. A four term polynomial model including x^3 (#7) resulted in a closer fit of the line to the data points, but the extrapolations were even more out of line. Statistical tests indicated that only the parameters b of the x term in the two equations was significantly different from zero. In a trial equation with the x^2 term deleted (#8) both the x and x^3 parameters were statistically significant, and the residual sum of squares value indicated a superior fit. However, the downward and upward extrapolations were also widely divergent.

DISCUSSION AND CONCLUSIONS

The graphical approximations of the two modified exponential equations (3 and 4) seem to indicate that these models would be adequate for practical purposes. Refinement of the parameters by log linear regression analysis and trial adjustment of the included transformation constants indicate that there is little to choose between them, the $y = b (x + k)^n$ model being perhaps superior (higher coefficient of determination and lower sum of squares of residuals). It is perhaps more logical to have the constant included in the term affected by the exponent. These models are consistent with a visualizable physical system in which the deposited stain size diverges at a smoothly increasing percentage rate with decrease in drop size from the predicted from an unevaporated drop of the same original size.

Examination of the downward extrapolations indicates drop diameter estimates that seem unreal as zero stain diameter is approached. However, the evaporative decay rate of a drop varies as the inverse of its diameter, and the smaller the drop, the longer it remains airborne and evaporating! It is therefore conceivable that a drop of appreciable original diameter could be reduced to a bit of dross that would fail to mark the surface, or, more likely, fail to impinge at all. Therefore the effect should be qualitatively real, at least for fluids containing very little non-volatile material. For fluids with appreciable non- or low-volatile content the stains made by very small drops will be more like those made by proportionately smaller drops of the non-volatile

components. For example a 'dried out' drop, originally 50 μm diameter with a residual non-volatile volume of 12.5% should make a stain the same size as a drop 25 μm diameter (i.e. $50^3 \cdot 125$) of the involatile fluid. Therefore the extrapolated line may be valid only until it approaches the simple exponential line characteristic of that involatile ingredient, displaced by the appropriate cube root factor.

Within the range of the primary data the polynomial equations appear to provide superior fitting lines. However, it seems that, as the number of terms in the polynomial is increased, the more the line is warped to fit the data points such that, in the limit, it may be forced through all of them without regard for how they may be randomly disposed about the 'physical' model, particularly when their number is small. This, along with the weakness of the extrapolations puts unto question the applicability of these models. They should be used only when the calibration data points encompass the full range of stain sizes found on the field sample cards.

For practical purposes there is not much to choose between the three modified exponential equations (No's 3b, 4b, 5 of Table II). However, equation 5 of which the model seemed to provide the best fit when used for a much more volatile formulation, and having the smallest sum of squares of residuals, probably gives the best estimate of the zero evaporation relationship. The equation for this line would have the same parameters as No. 5, but would lack the 'transformation' term:-

$$y_o = .450158 x_o^{.8761086}$$

From this we can postulate equations to match drops with any given residual

volume fraction (V_r) by dividing parameter b by $V_r^{1/3}$. In this case, V_r is estimated to be about 0.75, whence:-

$$y_r = .495463x_r^{.8761086}$$

This line meets the line of the $x:y$ plot from equation 5 at a point, where there is an abrupt change in slope. To provide a gradual transition to the $V_r = .75$ relationship an arbitrary negative term of the form x^m/k can be put into the equation such that the plotted line diverges from the $x_r : y_r$ line and is tangent to the $x:y$ line near the lower end of the primary data range. A suitable term was derived by trial and error to yield the equation:-

$$y = .495463 (x - x^4 / 4.11 \times 10^9)^{.8761086} \dots\dots\dots 5a$$

The line is tangent to the upper curve at 500 μ m stain diameter and becomes asymptotic to the $x_r : y_r$ line as the stain diameter is decreased. Accordingly, equation 5 should be used for stain sizes down to the point of tangency and equation 5a for stains below that point. The transition is scarcely evident in Figure I, but the need for it can be seen as the residual volume fraction decreases with increased volatility.

In theory, this extrapolation seems valid, but its accuracy depends on the correctness of the zero evaporation equation and our estimate of the short term residual volume fraction. This should match the maximum volume loss from spray drops falling from spray emission altitude at average ambient temperature. Comparing this estimated extrapolation line with the downward extensions of the six models (see Table III for comparison values), it is obvious that all except the simple exponential model (#2) grossly overestimate the sizes of the small drops. Bear in mind that the volume differential between two diameter values is equal to the cube of the ratio

of those diameters. Accordingly, they should not be used for drop size estimation below the range of the primary calibration data. The upward extrapolations of the three modified exponential models (3, 4 and 5) are fairly consistent. The linear model #1 overestimates the large drops whereas the exponential (direct log linear) model (#2) underestimates them. If the large drops do not constitute a significant portion of the drop deposit spectrum, and one is prepared to accept the relatively small plus and minus errors within the calibration range and the moderate overestimation inherent in the downward extrapolation; it seems reasonable to use the latter for general deposit volume analysis of spray sample cards, though not for drop size spectrum analysis. The discrepancies become larger with increased volatility of the spray formulation.

It should be pointed out that the size of the transformation or "evaporation compensation" terms in these equations is a function of the evaporative loss from the free surface of the fluid on the feed head of the drop generator. This is essentially inversely proportional to the fluid feed rate, as the surface area remains relatively constant. This is then homologous with the free surface to volume ratios of the drop produced at the various feed rates, each one being $\frac{1}{2}x$ or $2x$ the adjacent one. Loss by evaporation would be proportional to surface to volume ratio, which is also inversely proportional to the diameter of the free drop. The ratios on the feed mechanism are very high but the exposure time is short, whereas those of equivalent spray drops would be much lower but the exposure times much longer!

The effect of temperature on evaporation rates (via vapour pressure)

is such that a calibration curve (equation) appropriate for a given ambient temperature may give erroneous deposit estimates at higher or lower temperatures, particularly when the formulation contains a high percentage of more volatile components. At best the compensation for evaporative shrinkage can be only approximate.

Acknowledgements are due to Mr. A. Moore for useful discussions and computation of the parameters for the polynomial equations, and to Dr. A. M. Drummond for constructive criticisms.

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Table 1

Nominal mean vol. diam.		x Stain diam.	Equation No: 1	Estimated equivalent drop diameters y					
				2	3	4	5	6	
		0	27.51	0	15	17.05		20.65	
		20	30.87	8.15	20.21	21.36	34.1	24.40	
		40	34.24	14.33	24.77	25.57	33.1	28.14	
		80	40.97	25.20	33.34	33.77	37.44	35.60	
		160	54.43	44.31	49.40	49.55	50.74	50.41	
		305	78.83	74.94	76.79	76.80	76.88	76.84	
2	77	389	92.97+1.07	91.36 -.54	92.06 +.16	92.06 +.16	91.97 +.07	91.95 +.05	
①	91.9	432.3	100.25 +.45	99.56 -.24	99.81 +.01	99.81 +.01	99.69 +.11	99.67 -.13	
⑧	99.8	500	111.65	112.09	111.78	111.79	111.65	111.65	
⑧	125.8	581.8	125.41 -.39	126.71+1.01	126.05 +.25	126.07 +.27	125.96 +.16	126.00 +.20	
⑧	158.5	771	157.25-1.25	159.49 +.99	158.39 -.11	158.44 -.06	158.42 -.08	158.58 +.08	
		900	178.96	180.91	180.00	180.07	180.13	180.33	
⑧	199.7	1015.6	198.41-1.29	199.62 -.08	199.13 -.57	199.19 -.51	199.29 -.41	199.50 -.20	
		1200	229.44	228.68	229.24	229.28	229.43	229.44	
⑧	251.5	1339.5	252.91+1.41	250.11-1.39	251.73 +.23	251.73 +.23	251.88 +.38	251.57 +.07	
		1500	279.92	274.26	277.34	277.23	277.40	276.48	
8	316.9	1733.4*	319.20	308.54	314.14	313.98	313.97	311.65	
		1752 ⁺	322.33	311.24	317.05	316.88	316.86	314.40	
		2000	364.06	346.67	355.62	355.30	355.06	350.31	
		2500	448.20	415.77	432.10	431.36	430.48	418.41	
		3000	532.33	482.33	507.06	505.89	504.13	480.79	
Sum of Squares of Residuals			6.7142	4.2879	.4781	.4152	.3615	.1107	

0 Data base for the above equations, number = no. of cards measured for mean log diam.

* Possible bias in stain diameter measurement as most stains were irregular, and the more nearly circular ones selected for measurement probably averaged smaller than the true mean.

+ Estimate of more probable mean diameter.

Table II: Comparison of derived equations: coefficients of determination, and sums of squares of residuals.

Number	Equation	Coefficient of Determination R^2	Sum of Squares of Residuals
1	$y = 27.508 + 168276x$.9996497	6.7142
2	$y = .71005x^{.81448}$.9998996	4.2879
3	$y = 15 + .3435x^{.9077}$	-	.4781
3a	$y = 15 + .3392x^{.90959}$.9999838	.7691
3b	$y = 14 + .3382x^{.9025}$.9999854	.3498
4	$y = .3780 (x + 70)^{.8966}$	-	.4152
4a	$y = .37368 (x + 70)^{.89828}$.9999848	.4384
4b	$y = .391145 (x + 65)^{.892355}$.9999859	.3335
5	$y = .450158 (x + 325/x^{1/3})^{.876108}$.999987	.3615
6	$y = 20.6528 + .1872224x - .0000114895x^2$.9999943	.1107
7	$y = 23.4114 + .175932x + .0000035869x^2 - .0000000058267x^3$.9999985	.0289
8	$y = 22.7427 + .178768x - .00000000446557x^3$.9999983	.0418

Table III: Transformed stain diameters and equivalent drop diameters calculated from the equation:-

$$y = .495463 (x - x^4 / 4.11 \times 10^9)^{.8761086}$$

for comparison with the downward extrapolations of the equations in Table I.

Stain diam.	Transformed diam.	Calculated diam.
0	0	0
20	19.99996	6.84
40	39.999	12.55
80	79.990	23.03
160	159.84	42.24
305	302.89	73.94
389	383.43	90.91
500	484.79	111.65

FIGURE 1 : Prediction of drop diameters
from measured stain diameters

DROP DIAMETER μm

$$y = 450158 \left(x + \frac{325}{x^{1/2}} \right) \cdot 8761086$$

$V_r = 0.25$

$V_r = 0.50$

$V_r = 0.75$

$V_r = 1.0$

STAIN DIAMETER μm

50

100

200

500

1000

2000