

IMPACTS OF DIBROM® CONCENTRATE AND THREE NEW NALED FORMULATIONS ON THREE 1996 DU PONT AUTOMOTIVE PAINT FINISHES

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ABSTRACT. To investigate potential impacts on automobile finishes, droplets of 4 naled formulations were applied to 3 contemporary automotive paints and assessed by means of microscopic and unaided visual inspections. Three droplet size ranges simulated ground- and aerial-based ultra-low volume applications and were each generated for Dibrom® Concentrate, a new formulation of Dibrom Concentrate (VC-1088), and two other new naled formulations (Trumpet VC-1083 and Trumpet VC-1084). Du Pont automotive paint finishes tested were RK7072, RK8010, and RK7120 used on Ford trucks, General Motors cars, and Cadillacs, respectively. Visible spotting was never produced by small droplets averaging (SE) a volume median diameter of 13.12 μm (0.44), and quantifiable microscopic spots were detected only on the RK8010 paint finish. The latter paint finish was the most susceptible to spotting, whereas RK7072 was not affected by any formulation at each droplet size.

INTRODUCTION

The organophosphate insecticide naled is one of the leading adulticides used by mosquito control districts and other public health pest control programs in the United States. Naled is dispersed in the atmosphere as an ultra-low volume (ULV) spray to expose adult mosquitoes to drifting or falling droplets. Applications are frequently made in urbanized areas to reduce mosquito populations in peridomestic habitats. Although naled has the favorable attribute of a very short half-life in the environment (Tietze et al. 1996), its corrosiveness to metal and other substances has probably limited its success. This limitation is particularly evident when considering the potential for spotting of paint finishes on automobiles, boats, and recreational vehicles. Vehicles parked or driven in sprayed areas are normally exposed to ground-based and aerially produced droplets. It is of great consequence that such droplets conform to pesticide label specifications to ensure proper sizes are generated both for efficacy of mosquito suppression as well as safeguarding of private property (i.e., paint finishes). Specifications for nonthermal ground applications of Dibrom® Concentrate require that droplets not exceed 15 μm in mass median diameter (MMD), and that no droplet should be larger than 50 μm (Valent U.S.A. Corporation 1996). Aircraft applications must have no more than 5% of the droplets larger than 80 μm (Valent U.S.A. Corporation 1996).

Research and development at Valent U.S.A. Corporation recently created new formulations of naled targeting a product with lowered corrosiveness and eye irritation while retaining insecticidal efficacy. Similarly, new standards for automotive paint finishes are regularly introduced to that industry by Du Pont and De Nemours, recently with improvements in resistance to etching by acid rain and other types of corrosive atmospheric fallout.

This study assessed the effect of naled droplets,

simulating sizes produced by ground- and aerial-based ULV applications for Dibrom Concentrate, a new formulation of Dibrom Concentrate (VC-1088), and 2 other new naled formulations (Trumpet VC-1083 and Trumpet VC-1084), on 3 types of Du Pont automotive paint finishes, RK7072, RK8010, and RK7120, currently used on Ford trucks, General Motors cars and Cadillacs, respectively.

MATERIALS AND METHODS

Three size ranges of droplets were deposited on paint finishes using 2 droplet size separation techniques; larger droplets were generated using an "atomizer technique," and smaller droplets were generated within a settling chamber (Tietze et al. 1992). All paint panels were produced by Du Pont and De Nemours using the same "clear coat-base coat" technology used on commercially available vehicles. As a worst case scenario, all panels tested were black, a color believed to be most susceptible to spotting.

Large droplets were produced by spraying each compound across a horizontal surface in a closed room. About 1 ml of each compound was applied from a DeVilbiss no. 155 atomizer at a pressure of 15 p.s.i. for a duration of 5 sec using nitrogen as the propellant. Three paint panels (RK7072, RK7120, and RK8010) and two Teflon-coated slides (Vectec Inc., Orlando, FL) were exposed to settling droplets for 5 min postapplication at 2.5 and 4 ft. from the atomizer. Within 30 min of spraying, droplet volume median diameter (VMD) was assessed at a magnification of 200 \times using a Nikon 104 compound microscope and computed using Vec-tor droplet analysis software version 1.02a (Vectec Inc., Orlando, FL). Droplet calculations for each formulation were based on a spread factor of 0.69 (J. C. Dukes, personal communication). Droplet densities were assessed from the same slides

Table 1. Mean ranked visible spotting by medium-sized droplets of 4 Valent compounds on 3 types of Du Pont paint panels.

Panel type	Compound ¹			
	DC ²	VC-1083	VC-1084	VC-1088
RK7072	0.00b	0.00b	0.00a	0.00a
RK7120	0.33b	0.00b	0.00a	0.00a
RK8010	2.00a	1.00a	0.67a	0.33a

¹ Different letters indicate significant differences at the 0.05 level based on Student-Newman-Keuls procedure for mean separations.

² Dibrom Concentrate.

Table 2. Mean ranked visible spotting by large droplets of 4 Valent compounds on 3 types of DuPont paint panel.

Panel type	Compound ¹			
	DC ²	VC-1083	VC-1084	VC-1088
RK7072	0.00b	0.00b	0.00b	0.00b
RK7120	0.33b	0.67b	0.33b	0.67a
RK8010	2.00a	1.67a	2.33a	1.00a

¹ Different letters indicate significant differences at the 0.05 level based on Student-Newman-Keuls procedure for mean separations.

² Dibrom Concentrate.

based on 5 10-mm² counts, using the microscope calibrated stage and eyepiece micrometer. Paint panels were set aside for 24 h, then washed with a mild soap and dried with a nonabrasive cloth. Half of the exposed and washed panels were then waxed (Turtle Wax). This entire procedure was replicated 3 times per compound sprayed.

Smaller droplets were generated in a settling chamber (30 × 30 × 114 cm) as described by Tietze et al. (1992). The compounds were sprayed into the chamber using a J1A nozzle (Spraying Systems Co., Wheaton, IL) for 10 sec at 15 p.s.i., using nitrogen as a propellant. Panels and Teflon slides were exposed to settling droplets at the base of the chamber for 3 sec, starting at 29 and ending at 32 sec postapplication. Again, 3 replicates were made for each compound sprayed.

All treated panels were examined for visible and microscopic spotting. Visual assessments consisted of assigning ranks 0, 1, and 2 for no spotting, slight spotting, and heavy spotting, respectively. Visual assessments included both outdoor (sunlight) and indoor (fluorescent-light) inspections. Microscopic assessments were made at a magnification of 40× using a Nikon 104 compound microscope and fluorescent light source. When present, 50 spots were measured in diameter using an eyepiece micrometer, and density of spots was sampled within 4 swaths ranging from 7 to 20 mm².

Droplet sizes and frequencies were compared to determine whether droplet size groups used in the study were significantly different and whether droplet frequency varied between size groups.

Microscopic spotting and ranks were each compared between compounds and paint types for small, medium, and large droplet ranges using analyses of variance and Student-Newman-Keuls multiple range tests using SAS system on the Macintosh release 6.10 TS038 (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

Size (VMD) and density of droplets generated in tests did not vary significantly ($P > 0.05$) between compounds among small, medium, and large droplet size groups. Droplet VMD (SE) in small, me-

dium, and large size groups averaged 13.12 (0.44), 46.65 (0.79), and 71.10 (2.31) μm , respectively. Droplet densities (SE) in small, medium, and large size groups averaged 51.5 (9.07), 21.25 (2.40), and 24.27 (2.24) droplets/mm², respectively.

Visible spotting of paint finishes occurred in some of the large and medium droplet size groups, whereas such spots were never observed in the small size groups, regardless of compound or panel type. The panel type most susceptible to spotting was RK8010, which had significantly ($P < 0.05$) higher ranks compared with panels RK7072 and RK7120 when exposed to medium-sized and large droplets of Dibrom Concentrate, and VC-1083 (Tables 1 and 2). Although large droplets of VC-1084 yielded significantly ($P < 0.05$) higher ranks on RK8010 than on the other panel types, medium-sized droplets did not produce significantly different ranks between the 3 panel types. Similarly, large droplets of VC-1088 produced significantly higher ranked spotting on RK8010 and RK7120 compared with RK7072, whereas medium-sized droplets of that formulation yielded no difference in visible spotting between the 3 panel types. When comparing ranked degree of spotting between compounds generated by medium-sized droplets on RK8010 panels, Dibrom Concentrate caused significantly ($P < 0.05$) more visible spotting than VC-1083, VC-1084, and VC-1088. Large droplets on RK8010 panels yielded significantly ($P < 0.05$) less visible spotting using VC-1088 compared with Dibrom Concentrate and VC-1084 and VC-1083.

Microscopic spotting was apparent on panel RK8010 at all droplet size groups, whereas panel RK7120 had at times very faint spotting that was deemed "unquantifiable," and RK7072 never had microscopic spots. RK8010 panel spots were not significantly ($P > 0.05$) different in size when comparing between compounds at the large and medium droplet size groups (Table 3), whereas significant ($P < 0.05$) differences were detected when comparing compounds in the small droplet group. In the latter group, Dibrom Concentrate and VC-1083 did not spot finishes, and VC-1084 caused significantly ($P < 0.05$) larger spots compared with VC-1088. There was no significant ($P > 0.05$) dif-

Table 3. Average (\pm SE) spot diameter (μm) on paint finishes for 4 Valent compounds and on Du Pont paint finish RK8010.

Compound	Droplet size group		
	Small	Medium	Large
DC ¹	0.000 (—)	0.116 (0.014)a ²	0.166 (0.014)a
VC-1083	0.000 (—)	0.120 (0.007)a	0.161 (0.016)a
VC-1084	0.071 (0.004)a	0.141 (0.012)a	0.179 (0.006)a
VC-1088	0.055 (0.007)b	0.131 (0.014)a	0.157 (0.011)a

¹ Dibrom Concentrate.

² Different letters indicate significant differences at the 0.05 level based on the Student-Newman-Kuels procedure for mean separations.

ference in spot frequency on RK8010 panels when comparing compounds among droplet size groups.

In summary, on the basis of visible spot assessments and medium-sized ($\sim 46 \mu\text{m}$) droplets, Dibrom Concentrate caused the greatest spotting of the 4 formulations tested. The Du Pont paint finish RK8010 was most susceptible to visible spotting and was the only paint type yielding quantifiable microscopic spotting. There was an inconsistency to the above findings; small droplets sprayed on RK8010 produced microscopic spots that were largest for VC-1084 and VC-1088, whereas VC-1083 and Dibrom Concentrate did not spot that panel type.

Earlier tests using 1990 Du Pont paints and Dibrom-14 (unpublished data) did not yield microscopic spotting from droplets less than $24 \mu\text{m}$ in VMD. Those tests, however, were based on different paint standards by Du Pont as well as different droplet size ranges, making it difficult to make direct comparisons.

Preliminary recommendations for avoiding paint spotting would be the use of formulation VC-1088 (pending commercial availability) for aerial applications because it exhibited the lowest level visible effects at the largest droplet size range (VMD $\sim 71 \mu\text{m}$). At the medium droplet size range (VMD ~ 47

μm), VC-1088, VC-1083, and VC-1084 are recommended over Dibrom Concentrate. Although none of the formulations caused visible spotting at ground-based droplet sizes (VMD $\sim 13 \mu\text{m}$), Dibrom Concentrate and VC-1083 are recommended over VC-1084 and VC-1088 on the basis of microscopic assessments.

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