

## EFFECT OF ULV MALATHION ON AUTOMOTIVE PAINT FINISHES

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**ABSTRACT.** The relationship between malathion droplet size (VMD) and degree of damage to 1990, 1K and 2K General Motors paint standards was investigated in the laboratory and field. Laboratory tests indicated a positive correlation between malathion droplet VMD and damage spot size. Laboratory settling chamber tests revealed that size-thresholds of droplets too small to cause visible damage averaged 8 and 11  $\mu$  on washed 1K and 2K paints, respectively. Field tests indicated malathion caused no visible damage to 1K or 2K paint panels under routine operating conditions, although droplet sizes (VMD) sampled on the automobile surface averaged  $10.2 \pm 4.5$  and  $11.7 \pm 5.7 \mu$ . Microscopic damage was found on paint panels placed on the hood, roof, trunk and doors of the automobile when parked parallel or perpendicular to the course of the spray truck and when driven through the spray of a stationary spray truck.

## INTRODUCTION

Mosquito adulticides are routinely applied at ultra-low volume (ULV) rates in the U.S.A. As required by label, a specific droplet size distribution is needed to maximize the degree of insect control, and, at the same time, minimize potential damage to painted surfaces of automobiles and boats.

Production of optimum size insecticide droplets creates an adequate degree of drift, deposition and impingement for mosquito control (Johnston 1985). Droplet size restrictions are required for the use of mosquito adulticides such as Cythion® (malathion 91% AI) in ground application against mosquitoes in populated and rural areas (Cyanamid 1990). These directions state droplets should not exceed a mass median diameter (MMD) of 17  $\mu$ ; no more than 3% of the spray droplets may exceed 32  $\mu$ ; and no droplets are to exceed 48  $\mu$  (Cyanamid 1990). The intent of these droplet size restrictions is in part to prevent damage to automotive paint finishes as well as to produce other necessary spray characteristics.

Although the relationship between insecticide droplet size and its efficacy to kill adult mosquitoes has been well studied (LaMer et al. 1947, Yeomans 1949, Mount 1970, Mount and Pierce 1972, Lofgren et al. 1973), few studies have focused upon the relationship between droplet size and paint damage.

In this study, the relationship between malathion (91%) droplet size and degree of damage to two 1990 automotive paints was assessed in the laboratory. Field tests were also conducted to determine if these paints were damaged by malathion applied using standard ULV techniques during simulated automobile exposure scenarios.

## MATERIALS AND METHODS

Two types of laboratory tests were used to study the effects of malathion droplet size on automotive paints: the atomizer technique, and the settling chamber technique.

*Atomizer technique:* To measure droplet damage, malathion (Cythion 91%) was sprayed horizontally in a closed room measuring,  $4.5 \times 4.5 \times 3.05$  m. About 1 ml of malathion was applied from a De Vilbiss No. 155 Atomizer at a pressure of 15 p.s.i. for a duration of 10 seconds. Nitrogen was used as the propellant. The atomizer was fixed at the end of a 3.05 m board positioned horizontally 1.02 m above the floor. 1K (basecoat: 872-AB921; clearcoat: RK7103) and 2K (basecoat: 872-AB921; clearcoat: RK-7100) 1990 black paint standards measuring  $10 \times 15$  cm, were supplied by E. I. DuPont De Nemours and Company (DuPont, Troy, MI). Glass slides ( $2.54 \times 7.62$  cm) coated with Teflon (Vectec, Inc., Orlando, FL), and 1K and 2K paint panels, were each positioned along the board at distances of 0.61, 0.90, 1.22, 2.13 and 2.49 m from the atomizer. The paint panels were each divided into  $2.54 \times 10$  cm sections and individually exposed during separate tests. Droplets were allowed to settle for 5 min post-treatment. After 24 h, exposed panel sections were further subdivided and washed or washed and waxed. A covered section of each panel served as a control.

After 24 h post-treatment, slides were examined to determine the volume median diameter (VMD) and density of malathion droplets collected at each distance as described in Rathburn (1970). The droplet size spectrum for settled droplets was calculated using a computer program called Biomeasurement Droplet Analysis (Vectec, Inc., Orlando, FL) with a spread factor of 0.69.

The degree of damage to the paint panels was assessed as damage spot size and density per treatment and distance from the atomizer. Damage spot size was determined using a linear micrometer fitted in a Nikon 104 compound microscope at a magnification of 40X. One hundred spots were counted per panel. Damage spot density was measured with a 0.5 mm micrometer grid disc (Bausch and Lomb, Rochester, NY). Density was assessed by counting the number of squares encompassing 50 damage spots. This procedure was replicated 10 times per panel. In addition to the quantified measurement of damage to the panels, subjective ranks were assessed for each panel: 0—no damage, 1—microscopic damage and 2—visible damage.

The entire test was replicated 3 times and statistically analyzed by a multivariate analysis of variance and Student-Newman-Keuls multiple range test (SAS Institute 1985) to detect differences in size and density of droplets among distances from the atomizer, as well as between panel types. To determine the best predictor (variable) for damage size and density, stepwise regressions (SAS Institute 1985) were executed by panel type using a forward selection and pair-switching model selection method. Distance was converted to log-distance for the regression analysis. The regressors of the latter model were also checked for collinearity by producing eigenvalues and condition indices (SAS Institute 1985). To further interpret the relationship between droplet size and degree of damage, subjective ranks were plotted against droplet size.

*Settling chamber technique:* A settling chamber was used to produce malathion droplets smaller in size than those generated by the above technique. The chamber was constructed of Plexiglas plates, 30 × 30 × 114 cm. A removable Plexiglas panel 55 cm above the base divided the chamber into upper and lower sections. An aperture 5 cm from the top of the chamber admitted spray from a J1A nozzle (Spraying Systems Co., Wheaton, IL) (1/2 JJ body; J1650 fluid cap; J64 air cap) using nitrogen as a propellant. Malathion was sprayed into the upper portion of the chamber for 10 sec at a pressure of 15 p.s.i., the Plexiglas panel was then removed and a stopwatch was simultaneously initiated. Teflon-coated glass slides and 1K and 2K paint panels as described above were exposed to settling droplets at the following time intervals: 10 to 14, 30 to 38, 66 to 82, 138 to 170, 286 to 354, and 590 to 734 sec after removal of the Plexiglas panel. To facilitate this procedure, the glass slides and paint panels were placed on pages of paper, separated by blank pages, stacked in series so that exposed samples were easily removed

through a 4 cm high slot located at the base of the chamber.

Malathion droplet size was determined as described above. Due to the large number of droplets collected in the settling chamber, droplet density was determined using the micrometer disc grid technique described above for assessment of damage spot density. Settling rates were determined by dividing the droplet density by time of exposure.

This test was replicated 4 times and statistically analyzed as described in the horizontal droplet-size separation technique, only replacing log-distance with log-mean time interval.

*Simulated field trials:* To study the effect of malathion droplets on automotive paints in the field, tests were conducted at a local sod farm. A Leco 1600 Cold Aerosol Fog Generator (Lowndes Engineering Co. Inc., Valdosta, GA) was mounted onto a standard-size pickup truck and adjusted to deliver Cythion (malathion 91%) at a flow rate of 127 ml/min (4.3 fl oz/min) using a FMI pump (Fluid Metering, Inc., Oyster Bay, NY) and a pressure of 4.5 p.s.i. adjusted daily using a manometer. Ultra-low volume spraying was carried out during the early dusk period when wind speeds were below 16.1 km/h (10 mph).

Size and density of droplets and paint damage spots were sampled on slides and panels as described in the previous section. A 1989 Dodge Aries sedan was chosen as the target vehicle and 2 slides and one paint panel were taped to 5 general parts of the auto body: center of hood, center of roof, center of trunk lid, mid-line of right and left front doors. The first 3 sites were horizontal while the slides and panels on the doors were in a vertical orientation. Three treatment scenarios were tested: 1) curb-side parked auto, 2) head-in parked auto, and 3) drive through spray. In the curb-side parked treatment, the auto was parked parallel to and 1.52 m from the path of the spray head. In the second treatment, the auto was perpendicular to and about 4.57 m from the path of the spray head. In each of the first 2 treatments the spray truck was driven 16.1 km/h (10 mph) and the spray head was angled at 45%. In the last treatment, the spray truck was stationary and the sedan was driven through the fog at about 40.2 km/h (25 mph). It was necessary to set the spray head in an horizontal orientation on the drive through tests to lower the path of the spray cloud.

Due to time limitations, each type of panel was tested in a separate series of replications. The 2K panels were tested 3 times during April 1991, while 1K panels were tested 5 times from May to August 1991.

Droplet size was sampled prior to each field test by swinging a glass slide 7.62 m behind the spray head as described on the Cythion label (Cyanamid 1990) and by Rathburn and Boike (1977).

Paint panels were repeatedly exposed to applications of ULV-malathion to assess any cumulative effects. This was accomplished by progressively exposing  $2.5 \times 10$  cm sections of the panels used during replications of the above tests. Cumulative damage density and ranked degree of damage were assessed for each exposure.

A general linear models procedure (SAS Institute 1985) was used to statistically analyze the distribution of droplets and damage on the auto. Multivariate analysis of variance (MANOVA) was used to analyze differences among the dependant variables: droplet size, droplet density, damage spot size, damage spot density and ranked degree of damage. The dependent variables were analyzed between panel types, between treatment types (i.e., curb-side parked, head-in parked and drive-through) and between car parts (i.e., hood, roof, trunk, etc. . .). Student-Newman-Keuls multiple range tests were used to compare main effects. If droplet or damage spot densities were zero, then droplet sizes were indicated as missing. The climatological factors, air temperature, relative humidity and wind speed were recorded during each test.

## RESULTS AND DISCUSSION

The atomizer technique enabled us to collect a spectrum of droplet sizes ranging from 22 to  $65 \mu$ ; significant differences ( $P < 0.05$ ) in droplet size were detected with distance from the atomizer (Fig. 1). No significant difference in

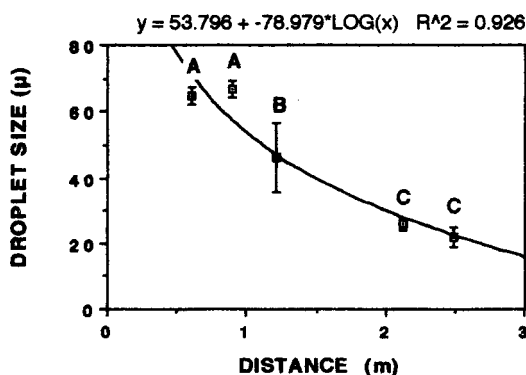


Fig. 1. Malathion droplet size (VMD) as a function of distance from atomizer. Different letters denote significant differences ( $P < 0.05$ ) as determined by Student-Newman-Keuls test. Bars indicate standard deviation.

droplet density was detected by distance from the atomizer due to variation between samples, but the distribution suggested the greatest density of droplets settled at about 1.75 m from the atomizer. Mean droplet densities  $\pm 1$  SD at 0.61, 0.90, 1.22, 2.13 and 2.49 m were  $8.91 \pm 2.55$ ,  $10.49 \pm 6.03$ ,  $12.60 \pm 3.28$ ,  $12.03 \pm 1.08$  and  $5.07 \pm 3.37$  droplets/mm<sup>2</sup>, respectively. Visible damage was found at each distance tested. When comparing damage size and density between panel types at separate distances, the only significant ( $P < 0.05$ ) differences detected were in damage densities at 1.22 m from the atomizer. Stepwise regressions indicated that the best predictor for damage size on both panel types was log-distance from the atomizer (Table 1). Damage spot density on 1K panels was best predicted by droplet density, while that on 2K panels was best predicted by droplet size (Table 1). Inspection of condition values generated from the collinearity test did not appear "ill-conditioned," and thus none of the regressors were removed from the model.

Settling chamber tests yielded droplets ranging from 6 to  $30 \mu$ . Significant differences ( $P < 0.05$ ) were detected between the first 3 sampling intervals, but little change occurred thereafter (Fig. 2). The settling rate of droplets changed significantly during the test, and the highest rate was measured at about 74 sec post-application (Fig. 2). The relationship between droplet size and damage size was linear for both 1K and 2K panel types (Fig. 3). When comparing damage spot size and deposition rate between panel types at different time intervals, significant ( $P < 0.05$ ) differences in rate of damage deposition were detected 74, 154 and 320 sec post-application. The best predictors for damage size and deposition rate on 1K panels were droplet size and droplet settling rate, respectively; on 2K panels damage size and deposition rate were best predicted by log-mean time interval of settling (Table 1). The settling chamber test yielded larger  $R^2$ s than the atomizer technique, perhaps due to less variation in droplet size and density. Collinearity tests did not reveal any "ill-conditioned" values and thus all the regressors were kept in the regression model.

Thresholds were apparent where droplet sizes caused changes from visible to microscopic and from microscopic to no damage. This was determined using "washed" and "washed and waxed," 1K and 2K paint panels (Fig. 4). After washing, the lower threshold for damage was about 8 and  $11 \mu$  for 1K and 2K panels, respectively; the lower threshold after washing and waxing was 8 and  $14 \mu$  for 1K and 2K panels, respectively.

Field tests indicated that no visible damage occurred to 1K and 2K panels when exposed to

Table 1. Best predictor variables for damage size and density on 1K and 2K General Motors paint panels using stepwise regression in 2 testing strategies

| Dependent variable | Best predictor variable by paint type |                |        |                    |                |        |
|--------------------|---------------------------------------|----------------|--------|--------------------|----------------|--------|
|                    | 1K                                    |                |        | 2K                 |                |        |
|                    | Variable                              | R <sup>2</sup> | P      | Variable           | R <sup>2</sup> | P      |
|                    | <i>Atomizer technique</i>             |                |        |                    |                |        |
| Damage size        | LDIST <sup>1</sup>                    | 0.47           | 0.0005 | LDIST              | 0.51           | 0.003  |
| Damage density     | DPDEN <sup>2</sup>                    | 0.11           | 0.22   | DPSZ <sup>3</sup>  | 0.02           | 0.59   |
|                    | <i>Settling chamber technique</i>     |                |        |                    |                |        |
| Damage size        | DPSZ                                  | 0.71           | 0.0001 | LTIME <sup>4</sup> | 0.65           | 0.0001 |
| Damage depos. rate | DPDEN                                 | 0.39           | 0.001  | LTIME              | 0.36           | 0.002  |

<sup>1</sup> LDIST = Log10\* (distance from atomizer).  
<sup>2</sup> DDPEN = malathion droplet density.  
<sup>3</sup> DPSZ = malathion droplet size in microns.  
<sup>4</sup> LTIME = Log10\* (mean time interval post-application).

ULV malathion under simulated application scenarios. Microscopic damage was detected on both panel types during each treatment.

Teflon slide VMDs averaged 14.0 and 14.9 μ during 1K and 2K tests, respectively. Droplet sizes on slides attached to the automobile averaged 10.2 and 11.7 μ on 1K and 2K panels, respectively. Both samples showed no significant difference (P > 0.05; t-test) in droplet size

between the 2 series of tests. Each application of malathion conformed to Cythion label requirements for droplet size.

When comparing treatments (curb-side parked, head-in parked and drive through), during the 1K series significantly smaller (df = 2; F-value = 5.9; P < 0.05) droplet sizes were found on drive-through slides than on the head-in and curb-side parked treatments. Increased impinge-

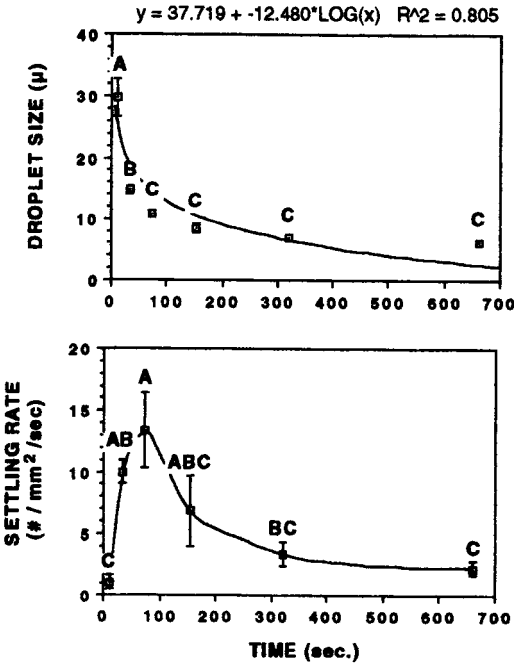


Fig. 2. Malathion droplet size (VMD) and settling rate as a function of settling time. Different letters denote significant differences (P < 0.05) as determined using Student-Neuman-Keuls test. Bars indicate standard deviation.

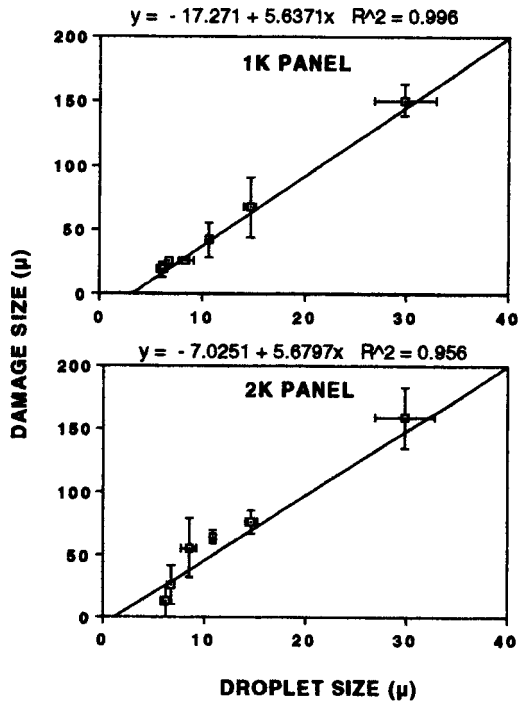


Fig. 3. Malathion damage spot size by droplet size on 1K and 2K paint panels determined using settling chamber tests. Bars indicate standard deviation.

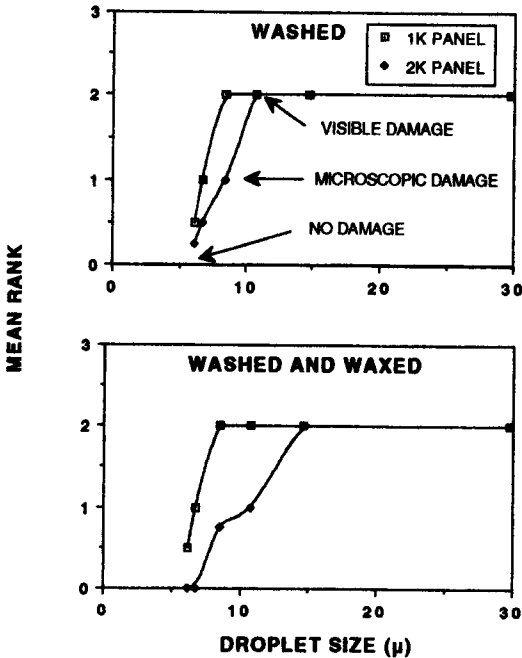


Fig. 4. Ranked degree of damage to 1K and 2K paint panels by malathion droplet size (VMD) using washed and washed and waxed panels.

ment of smaller droplets may have produced this result. During both 1K and 2K series, the drive-through treatment had significantly (1K:  $df = 2$ ;  $F\text{-value} = 3.6$ ;  $P = 0.033$  and 2K:  $df = 2$ ;  $F\text{-value} = 6.2$ ;  $P = 0.004$ ) higher densities of droplets compared with the two stationary treatments. Again, this was probably due to increased impingement. Comparing 1K and 2K panels indicated that 2K panels had higher densities of droplets and damage spots as well as larger damage spots than 1K panels. These spots, however, were always invisible to the unaided eye.

No significant differences ( $P > 0.05$ ) were detected in droplet or damage, density and size when they were compared between car parts (i.e. hood, roof, trunk, etc. . .).

Droplet sizes collected on field test slides (Table 2) were similar to the laboratory-determined damage threshold values (Fig. 4). Droplet densities, however, were much lower in field tests when compared with that of those in the laboratory. It is hypothesized that such differences may have altered the paint damage threshold (i.e., less visible damage at slightly larger droplet sizes), since both droplet size and density contribute to this subjective ranking.

Repeated applications caused increases in the density of damage spots, but even after a maximum of 5 exposures to ULV malathion, no visible damage was detected on 1K paint panels.

Increases in damage spot density were more regular during the 1K series than the 2K series. The reason for this is still unclear.

Weather conditions during the 2 series of tests were similar regarding relative humidity and wind speed but slight differences were evident for temperature due to seasonal progression. During 2K tests in April, the relative humidity averaged  $\pm 1$  SD,  $93.8 \pm 5.0\%$  and wind speeds averaged  $6.7 \pm 1.2$  km/h. During 1K tests, conducted from May to August, relative humidity and wind speeds averaged  $94.5 \pm 3.3\%$  and  $4.3 \pm 3.7$  km/h, respectively. Temperatures averaged  $25.1 \pm 2.5$  and  $22.0 \pm 2.0^\circ\text{C}$  during the 1K and 2K tests, respectively.

Rathburn and Boike (1977) exposed earlier paint standards to ULV malathion sprays using 6 different aerosol generators in the field. They found the Leco HD produced a VMD of  $13.5 \mu$  when sampled 7.62 m from the spray head. They also reported that after polishing, microscopic damage was present on all paint panels at a magnification of  $10\times$ . The results of the current study are in accord with those of Rathburn and Boike (1977) regarding both droplet size and degree of damage observed.

Differences in droplet sizes recovered using the 2 field collection techniques, hand-waved slide and slides attached to parked or moving vehicle may be in part due to inherent droplet size collection biases. Since the velocity of the slide will influence impingement efficiency (Carroll and Bourg 1979), collection on moving surfaces (i.e., waved slide or slide on moving vehicle) should have sampled a greater proportion of the smaller-sized droplets. This was true when comparing droplet sizes on the moving versus the parked treatments during the 1K series. However, droplets averaged larger sizes when collected using the hand waved slide method compared with slides taped to the automobile surface. One reason for this discrepancy may be greater settlement time on the automobile-based samples and thus collection of a greater proportion of smaller droplet sizes. Another hypothesis for this difference is that laminar flow effected droplet behavior around the automobile, compared with little laminar flow around the waved slides. Further study is needed to understand the relationship between degree of laminar flow and collected droplet sizes.

Although "damage" may be a subjective quality, it is most likely caused by a combination of droplet size and density, as well as insecticide and solvent type. Future attempts at modeling the relationship between insecticide droplets and paint damage will need to focus upon the effects of droplet density under laboratory and field conditions.

Table 2. Droplet size and density sampled on glass slides and average damage spot size and density sampled paint panels, both of which were exposed on automobile surfaces to ULV malathion treatments during 2 test series

|                                   | Droplet <sup>1</sup> |                                | Damage spot <sup>1</sup> |                                |
|-----------------------------------|----------------------|--------------------------------|--------------------------|--------------------------------|
|                                   | Size ( $\mu$ )       | Density (no./mm <sup>2</sup> ) | Size ( $\mu$ )           | Density (no./mm <sup>2</sup> ) |
| <i>1K paint panel test series</i> |                      |                                |                          |                                |
| Curbside                          | 11.9 $\pm$ 4.6       | 0.06 $\pm$ 0.07                | 104.2 $\pm$ 63.0         | 0.004 $\pm$ 0.007              |
| Head-in                           | 11.4 $\pm$ 4.6       | 0.02 $\pm$ 0.03                | 83.5 $\pm$ 35.0          | 0.007 $\pm$ 0.006              |
| Drive                             | 7.9 $\pm$ 3.5        | 0.08 $\pm$ 0.09                | 89.2 $\pm$ 50.0          | 0.007 $\pm$ 0.010              |
| <i>2K paint panel test series</i> |                      |                                |                          |                                |
| Curbside                          | 13.4 $\pm$ 6.6       | 0.06 $\pm$ 0.08                | 125.9 $\pm$ 27.9         | 0.007 $\pm$ 0.008              |
| Head-in                           | 10.4 $\pm$ 6.2       | 0.08 $\pm$ 0.10                | 150.4 $\pm$ 35.2         | 0.018 $\pm$ 0.041              |
| Drive                             | 11.1 $\pm$ 4.0       | 0.25 $\pm$ 0.25                | 104.6 $\pm$ 26.6         | 0.061 $\pm$ 0.064              |

<sup>1</sup> Average  $\pm$  1SD.

In conclusion, field simulations of ULV malathion sprays caused microscopic damage to modern automotive paint finishes, but no visible damage could be detected. However, laboratory tests producing larger droplet sizes and higher droplet densities caused visible damage to these paint finishes.

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