## Introduction

More than 1,000 domestic textile processing sites have been identified where dyeing or printing operations may occur. Dye weighers in textile dyeing and printing facilities are involved in the weighing and transfer of relatively small quantities of numerous powder dyes and other dye chemicals. This results in potential exposure to a diverse range of chemicals which exhibit a broad spectrum of toxicological properties. The Textile Dye Weighing Monitoring Study (TDWMS), a cooperative venture between the U.S. Environmental Protection Agency (EPA), the American Textile Manufactures Institute, Inc. (ATMI), and the Ecological and Toxicological Association of Dyestuffs Manufacturing Industry (ETAD), including a survey of 24 randomly selected textile dyeing or printing sites which used powder dyes. At each site, dye weighers were observed for an 8 hour shift; personal monitoring and area sampling data were taken. Certified industrial hygienists recorded worker activities, duration of potential exposure, personal engineering controls in use, and quantities and frequency of use of each dye that was handled during the monitoring period. The particulates collected on the air monitoring filters were analyzed for commercial dye content using a spectrophotometric method developed for the study. The study provides the most comprehensive review ever under taken of textile worker exposure to powder dyestuffs.



10/15/92

Background

Prior to the TDWMS, the available data on potential exposure levels of workers associated with the weighing or mixing of powder dyes were limited, and they were not always representative of textile dyeing operations. Upon completion of the TDWMS, the Chemical Engineering Branch (CEB/ETD) developed an assessment methodology for chemicals evaluated under the New Chemicals Program (PMNs). This assessment permits the engineer to calculate an average and worst case worker exposure (Heath, 1988). This approach is adequate as a first step, but is not possibly the best use of all the TDWMS data as it takes the average of the data for use as the average exposure and the highest exposure value obtained in the study for use as the worst case exposure. Therefore, this assessment methodology is being revised using a statistical analysis of the data.

Due to the small number of data points (24), it is very difficult to make a statistically precise estimate for upper percentile values of the distribution of all exposure measurements. From an examination of the plot of the 24 data points, there was a clear indication that the distribution of exposure measurements is positively skewed (that is skewed to the right). An exponential distribution model was chosen as the basis for calculation of an upper percentile tolerance interval. The exponential model was chosen because it tends to provide a reasonable approximation to the shape of the distribution and can produce the tolerance interval which was desired. With a tolerance interval, it is possible to specify with a prescribed level of confidence that no more than a given percentage of a distribution falls above a certain point. For example, it is possible to state that we have a 95% confidence that no more than 10% of the measurements of a distribution will fall above a given value. The actual confidence level and percentage of the distribution which we use can be chosen according to our specific requirements.

A. Occupational Exposures

The Textile Dye Weighing Monitoring Study (TDWS) was a joint project between industry and EPA to obtain exposure data for dye weighing rooms (drug rooms) of textile wet processing plants. Twenty-four (24) sites were selected randomly from a list of 1,390 textile facilities thought to use powder dyes. The objective of the study was to estimate the distribution of dye concentrations in dye weigher's breathing zone in a statistically valid manner. The twenty-four personal samples showed an arithmetic mean of 0.18 $mg/m^3$ of total dye with a standard deviation of 0.26 $mg/m^3$. The maximum and minimum data points were 0.013 $mg/m^3$ and 1.20 $mg/m^3$ respectively. The study also revealed that on average 1-2 workers are exposed per shift and typically 3 shifts per day.

The reasonable worst case exposure will be calculated using the data from the Textile Dye Weighing Monitoring Study. The data collected in the study represents the exposure measured from two personal monitoring devices on dye weighers at 24 sites. Initially, the Chemical Engineering Branch selected the highest data point to represent the "reasonable worst case" exposure. This is not the best estimate of what would be the "reasonable worst case" exposure. To represent the "reasonable worst case" expected, the point was selected such that there was 95% confidence that no more than 10% of the data was greater than this value. Therefore, the "reasonable worst case" exposure can be calculated using 0.161 mg/kg of dye weighed. This value was calculated assuming an exponential distribution, because the data was skewed when graphed. The skewed graph differs from the normal or bell-shaped curve, where both halves are symmetrical. This graphed represented a skew to the higher exposures or to the right. The exponential distribution assumption simplifies the calculations; only one parameter is needed to describe this curve, hence, the arithmetic mean equals the standard deviation. The average (typical) exposure will be based on the mean of the data collected from the TDWMS. Therefore, the typical inhalation exposure can be obtained by using 0.0477 mg/kg of dye weighed. The inhalation exposures are calculated utilizing the average and the "reasonable worst case" data (mg/kg of dye weighed) and multiplying it by dye strength (% PMN) and amount of used per dye lot (kg used/dyelot). Both average and "reasonable worst case" exposures should be provided in the occupational exposure assessment.

For liquid dyes, the inhalation exposure should be based on standard CEB models using the vapor pressure. Therefore, inhalation exposure during weighing of a liquid dye is expected to be negligible as most liquid dyes are non-volatile.

Dermal exposures will be calculated using one hand incidental contact of 650 to 1,950 mg/day of total dye formulation. This data was obtained for weighing, scooping and mixing powders such as used in dye drug room operations. Thus, the dermal contact is estimated by multiplying exposures by dye strength.

B. Environmental Releases to Water

Releases to water during dyeing of textiles may result from a number of areas (e.g. dropping the dye bath). These releases can be estimated by selecting the appropriate degree of exhaustion from the following table.

| Dye Type | Degree of Exhaustion |
|---|---|
| Acid | 80% |
| Acid Metallized | 80% |
| Basic | 90% |
| Chrome | 80% |
| Direct | 70% |
| Naphthol | 75% |
| Neutral Premetallized | 90% |
| Reactive | 60% |
| Vat | 75% |
| Disperse* | 75-95% |

*A single degree of exhaustion can not be used for disperse dyes. The degree of exhaustion for a dye depends on the fabric being treated (e.g. acetate or polyester), the dye bath temperatures and the type of dyeing equipment.

The release to water is obtained by multiplying the daily usage (kg/site-day) by the unexhausted percentage of dye. The exhausted percentage of dye is calculated taking the difference of the degree of exhaustion (e.g. 80%) and 100%. The calculation of number of days per year and the number of sites will be discussed in the next sections.

Engineering Assessment of Textile Dyes

In a PMN the dye to be assessed will typically contain information on the color (e.g. black), the type (e.g. acid), the production volume (e.g. PV = 10,000 kg/yr), and the dye strength (i.e. PMN% = 45). From this initial information supplied in the Premanufacture Notice (PMN) submission, the engineer is required to supply the occupational exposure (e.g. inhalation = 0.14 - 0.98 mg/ day and dermal = 293 - 878 mg/day) and environmental releases (e.g. amount to water = 1.3 - 1.96 kg/site-day). In order to obtain these essential parts of the assessment, it is necessary to obtain the amount used per site-day, the number of annual operating days, the number of sites, the number of workers, etc.

The first task is to estimate the daily dye usage. Some basic assumptions are made to obtain the dye usage. Typically, 1,000 pounds of fiber per dyelot is used, along with 1% on the weight of fiber (owf) (unless, it is a heavy depth shade, like a black or brown, then 5% owf is used instead). These assumptions are used with the dye strength (%PMN) to calculate amount used per dyelot. Next the number of dyelots per day are calculated. This may vary depending type of operation (e.g. batch or continuous) and the number of hours per dyelot (typically, 6 hrs for batch and 8 hrs for continuous). Thus, the amount of dye used (kg) per site-day can be obtained by multiplying amount used per dyelot by number of dyelots per day.

Calculating the number of annual operating days can be achieve by dividing the amount purchased per site-year (typically, 1,000 kg/site-yr) by the amount used per day.

The number of sites is obtained by dividing the production volume (PV) or import volume (IV) by the amount purchased per site-year.

SUBJECT: Textile Dyes

EXAMPLE: Old Method (Heath, 1988)

Given: PV of 10,000 kg, a brown acid dye, used at 45% concentration.

Calculate amount of dye used per site-day:

$$1000\frac{lb\ fiber}{dyelot} \times 5\%\ dye\ owf \times 45\%\ dye\ strength = 22.5\frac{kg\ used}{dyelot}$$

Assume: 6 hrs/dyelot (for batch) but, 8 hrs/dyelot (for continuous)

$$24\frac{hrs}{day} \times \frac{dyelots}{6\ machine\text{-}hrs} \times \frac{1\ dye\ machine}{site} = 4\frac{dyelots}{site\text{-}day}$$

Therefore,

$$22.5\frac{kg(used)}{dyelot} \times 4\frac{dyelots}{site\text{-}day} = 90\frac{kg(used)}{site\text{-}day}$$

Assume: 1,000 kg PMN purchased/site-yr

Calculate number of days per year:

$$1000\frac{kg\ PMN\ purchased}{site\text{-}yr} \times \frac{site\text{-}day}{90\ kg\ used} = 11\ \frac{days}{yr}$$

Calculate number of sites:

$$10000\frac{kg}{yr} \times \frac{site\text{-}yr}{1000\ kg} = 10\ sites$$

Releases to water:

$$90\frac{kg(used)}{site\text{-}day} \times [1 - (80\%\ degree\ of\ exhaustion)] = 18\frac{kg(released)}{site\text{-}day}$$

Check of release estimate to water:

$$18\frac{kg(released)}{site\text{-}day} \times 11\frac{days}{yr} \times 10\ sites = 1980\frac{kg(released)}{yr}$$

$$1000\frac{kg}{yr} \times [1 - (80\%\ degree\ of\ exhaustion)] = 2000\frac{kg(released)}{yr}$$

SUBJECT: Textile Dyes

EXAMPLE: New Method

From the data collected during TDWMS:

The ratio of the amount of dyes weighed by the number of dyes weighed (mean) = 3.64 kg/shift

The ratio of the amount of dyes weighed by the number of dyes weighed (95% tolerance interval for the top 5%) = 17.90 kg/shift

The number of shifts = 2 - 3/day

Calculate amount of dye used per site-day:

Typical (Mean) =

$$3.64 \frac{kg(total)}{shift} \times 2-3 \frac{shift}{day} = 7.3-10.9 \frac{kg(used)}{site\text{-}day}$$

Worst Case =

$$17.90 \frac{kg(total)}{shift} \times 2-3 \frac{shift}{day} = 35.8-53.7 \frac{kg(used)}{site\text{-}day}$$

Assume: 1,000 kg PMN purchased/site-yr
Calculate number of days per year:

$$Typical: 1000 \frac{kg\ PMN\ (purchased}{site\text{-}yr} \times \frac{site\text{-}yr}{7.3-10.9\ kg(used)} = 137-92 \frac{days}{yr}$$

$$Worst\ Case: 1000 \frac{kg\ PMN\ (purchsed)}{site\text{-}yr} \times \frac{site\text{-}yr}{35.6-53.7\ kg(used)} = 28-19 \frac{day}{yr}$$

Calculate number of sites:

$$1000 \frac{kg}{yr} \times \frac{site\text{-}yr}{1000\ kg} = 10\ sites$$

Releases to water:

$$Typical: 7.3-10.9 \frac{kg(used)}{site\text{-}day} \times [1-(80\%\ degree\ of\ exhaustion)]$$
$$= 1.5-2.2 \frac{kg(released)}{site\text{-}yr}$$

$$WorstCase: 35.6-53.7 \frac{kg(used)}{site\text{-}day} \times [1-(80\%\ degree\ of\ exhaustion)]$$
$$= 7.1-10.7 \frac{kg(released)}{site\text{-}day}$$

Occupational Exposure:
Inhalation: Old Method

**Worst Case (for powder dye):**

$$exposure\ (mg/day) = \frac{0.170\ mg}{weighing} \times \%conc. \times \frac{no.\ of\ weighings}{day}$$

$$= \frac{0.170\ mg}{weighing} \times 45\%\ conc. \times \frac{4-12\ weighings}{day} = 0.31-0.92\ \frac{mg}{day}$$

**Average Case (for powder dye):**

$$exposure\ (mg/day) = \frac{0.0314\ mg}{weighing} \times \%conc. \times \frac{no.\ of\ weighings}{day}$$

$$= \frac{0.0314\ mg}{weighing} \times 45\%\ conc. \times \frac{4-12\ weighings}{day} = 0.06-0.17\ \frac{mg}{day}$$

The number of weighings of each PMN is a personal judgement based on mass used per site and conditions of use (see Heath-1984(Mar)). Typical figure follow:

| Type of Operation | No. of Dyeing Units in Operation/Site-day | No. of Dyelots per Shift/Unit | No. of Weighings per Dyelot |
|---|---|---|---|
| Batch | 3 | 1.33 | 1 - 3 |
| Continuous | 1 | 1 | 3 - 4 |
| Print | 1 | 1 | 2 - 4/screen |

Assume: 3 shifts/day and 1 dyelot/shift

**Inhalation: New Method**

**Worst Case (for powder dye):**

$$0.161\ \frac{mg}{kg(weighed)} \times 45\% \times 35.6-53.7\ \frac{kg(used)}{dyelot} = 2.58-3.89\ \frac{mg}{day}$$

**Average Case (for powder dye):**

$$0.0477\ \frac{mg}{kg(weighed)} \times 45\% \times 7.3-10.9\ \frac{kg(used)}{dyelot} = 0.16-0.23\ \frac{mg}{day}$$

Therefore, inhalation is expected to be at worst 2.58-3.89 mg/day and typically 0.16-0.23 mg/day.

Dermal:

From Engineering Manual, weighing powder/scooping/mixing as in dye drug room would produce incidental contact of 650 to 1,950 mg to one hand.

$$650 - 1950 \frac{mg}{day} \times 45\% \, dye \ strength = 293 - 878 \frac{mg}{day}$$

Therefore, dermal exposure is expected to be 293 - 878 mg/day.

## REFERENCES


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(4) **MEMORANDUM** prpared by Dan Reinhart, Math Statistician, Design and Development Branch, Exposure Evaluation Division, Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Washington, D.C.

APPENDIX I: Calculation of Tolerance Interval for Upper End of Exponential Distribution[4]

- It is often very difficult to make precise estimates about extreme values of a distribution where there is limited data and little is known about the shape of the population distribution. In this situation, it is necessary to make the same assumptions about the distributional model which best characterizes the measurements under consideration. In this case, this is a highly speculative undertaking.

- EPA decided that a tolerance interval for an upper end proportion of the distribution was preferred versus a point estimate for the upper end of the distribution (e.g., 95% confidence that no more than 10% of the distribution falls above a prescribed point versus the point estimate of the 90th percentile). The distinction between these two types of estimates must be understood. That point for which we have 95% confidence that no more than 10% of the distribution well exceed corresponds to the point estimate for the 96.5th percentile (n = 24). 95% confidence for the top 5% translates to the point estimate for the 98.7th percentile.

- Typically, EPA uses a lognormal distribution model to characterize monitoring data. An exponential distribution model was selected based on the following factors: (1) the sample data was positively skewed, although the extent of the skew in the data was extreme as in the exponential; (2) the exponential distribution with a single parameter (mean = standard deviation) is relatively easy to use for the purpose of calculating tolerance intervals; (3) the use of the lognormal model can result in extreme values when calculating point estimates and tolerance intervals for the high end of the distribution.

Steps in Calculating of Tolerance Interval Based on Exponential Distribution Model

- Since the sample mean was smaller than the sample standard deviation and the proportion of the distribution above the sample mean was larger than the exponential distribution, an adjustment in the measurement scale was imposed to render the sample statistics more consistent with the exponential model. Essentially, this adjustment was made by noting how much greater the mean would have to be in order to have approximately 37% of the sample data fall above it (as is the case with the exponential). This adjustment also produced a mean which was much closer to the sample standard deviation.

- Using statistical information that the sample mean of an exponential distribution is distributed $X = X_{2N}/2n(0)$, a one-side upper 95% connfidence interval for 0 (the population parameter) for the exponential distribution was calculated. In this particular case, with 24 measurements, it is determined that no more than 5% of the time (95% confidence) will the population mean exceed 1.450 times the sample mean. So to find the upper 95% confidence bound for the population mean, the sample mean was multiplied by 1.450.

- For an exponential distribution, the point which cuts off the top ten percent of the distribution is 2.303 parameters (standard deviations) from the origin or 2.303 times larger than the mean (mean = standard deviation). By multiplying the upper 95% confidence bound for the population parameter (0 = 1.450 X) by 2.303, the 95% tolerance interval for the top 10% of the distribution is calculated. So three figures play a part in this calculation. (1) The adjustment of the sample statistic (mean) to make it more characteristic of an exponential distribution, (2) the multiplier needed to convert the sample mean into the upper 95% confidence bound for the population mean, and (3) the point (2.303 times the estimate for the mean) that defines the top 10% of the exponential distribution.

- By multiplying the adjusted sample mean by 1.450 x 2.303, we find that point that we are confident no more than 10% of the distribution will exceed.

ESTIMATION OF HIGH END TOLERANCE INTERVAL
FOR AVERAGE WEIGHT PER DYE

MAJOR POINTS

* Examination of the distribution of the average weight per dye (total weight/number of dyes) for 24 locations reveals that the distribution is highly skewed in the positive direction and conforms to the general shape of an exponential distribution model. Comparison the relative frequencies from the sample histogram to the expected frequencies based on the exponential model show a very good fit, Also, the mean (3.64) and standard deviation (4.27) of the sample are relatively close to one another which is also compatible with the exponential distribution model. For these reasons, an exponential model will be used to calculate a upper bound tolerance interval with these data.

* One of the problems with employing an exponential model is determining the value of the single parameter that represents both the mean and standard deviation of the exponential distribution. Several alternatives are possible. The value of the parameter may be estimated by: (1) using the mean of the sample data, (2) using the arithmetic average of the sample mean and standard deviation, (3) using a combination of the sample mean (counted once) and sample standard deviation (counted k-1 times). The three solutions suggested above are not exhaustive; they are only intuitive and arbitrary ways to deal with this problem. It is clear that the closer the sample mean and standard deviation are to one another, the less critical this problem becomes. In the present case, the two measures are relatively close, so the decision of how to deal with this issue will not greatly effect the calculated tolerance interval.

* Using a combination of the sample mean (counted once) and the sample standard deviation (counted k-1 times) appears to be a very reasonable approach. It is generally consistent with other statistical approaches and yields results which are similar to other estimation methods. An explanation of the calculation for the k-factor which is used to define the tolerance interval is included.

For a sample 24 measurements and a 95% tolerance interval for the top 10% of the distribution, the k-factor is found to be 3.34. That is, the point in an exponential distribution that defines the 95% tolerance interval for the 10% of the measurements is 3.34 parameters from the origin. The present case, using both the sample mean and standard deviation, the critical point is 2.34 standard deviations above the mean. This works out to be **13.63**. The point for a 95% tolerance interval for the top 5% is **17.90**.

SUBJECT: CALCULATION OF HIGH END TOLERANCE INTERVAL FOR EXPONENTIAL DISTRIBUTION USING SAMPLE MEAN

* Let $\theta$ represents the real but unknown value of the population parameter (mean = std. dev.) of an exponential distribution.

* Let $\bar{X}$ represent the arithmetic sample mean calculated from n randomly selected sample measurements (from this exponential distribution).

* It is known that $2n\bar{X}/\theta$ is distributed $x_{2n}$. So, $\bar{X}/\theta = x_{2n}/2n$

  or $\theta/\bar{X} = 2n/x_{2n}$

* Understanding the relationship between the population parameter, $\theta$, which is fixed but unknown, and the sample mean (X) which is random variable (because it varies depending on the specific sample which is selected) is very important in the calculation for the tolerance interval.

Based on this relationship, it is possible to calculate an upper, one-sided confidence interval for $\theta$ using the sample mean, . More useful for the present task, it is possible to calculate a confidence proportion relating X to $\theta$. For example, using a table of chi-square ($x^2$) distribution values, it is possible to show that with a sample of, say, twelve (n=12) we are 95% confident that the sample mean (X) will be no smaller 13.67/24 or 57% of $\theta$. (13.67 comes from Chi-Square Table with 24 degrees of freedom and .05 probability of obtaining a Chi-Square values smaller than this value. 24 is 2n, twice the number of observations in the sample.) Conversely, we are 95% confident that the unknown value of the population parameter ($\theta$) is no greater than 175.6% (1.765) of the sample mean calculated from twelve randomly selected sample measurements.

* Based on the characteristics of the exponential distribution, it is also known that only 10% of the measurements (area in the tail) of the distribution exceed the point which is 2.303 $\theta$ above the origin of the distribution. Only 5% exceed the point that is 2.996 x $\theta$. Only 1% exceed 4.605 x $\theta$ (See Table). If the actual value of $\theta$ were known, the precise point that defined whatever percentage of the distribution we wished too prescribe could easily be determined. Since $\theta$ is unknown, the sample mean may be used to estimate it. Recalling that the sample mean varies depending on the actual sample selected, using a one-sided confidence interval to estimate the probable value of $\theta$ is reasonable.

* Therefore, to create, say, a 95% tolerance interval for the top 10% of the distribution (assuming it is exponential), first, multiply the sample mean (X) based on, say, 12 measurements by 1.756 (175.6%) to be 95% certain that the value of $\theta$ is not being underestimated. This product would be multiplied by 2.303. The

resulting product is 4.044. With a sample of 12 measurements, the sample mean multiplied by 4.044 will yield the value that we are 95% confident will be exceeded by no more than 10% of the measurements of the distribution.

STEPS FOR THE CONSTRUCTION OF TOLERANCE INTERVAL

Step #1

Using the Chi-Square Distribution table, first find the Chi-Square value associated with 2n degrees of freedom and the probability (of obtaining a value of $x^2$ smaller than table value) of 1-[the confidence level of the tolerance interval]. For example if 8 sample measurements were used to calculate the mean, and we wished to have a 90% confidence level for the tolerance interval, the value associated with 16 degrees of freedom and .01 (1 - .90) probability would be used. (That number from the Chi-Square table is 9.31.)

Step #2

Next, twice the number of sample measurements (2n) is divided by the Chi-Square value from the table. For the above example, 2n or 16 is divided by 9.31 to yield 1.72. This means that we can be 90% confident that the real (unknown) value of the population parameter, $\theta$, is no larger than 1.72 times the sample mean calculated from the 8 sample measurements.

Step #3

Next, it is necessary to determine the multiplier of $\theta$ required to cut off the top portion of the exponential distribution equal to the area the tolerance interval is intended to describe. For example, if it is desired that the tolerance interval apply to the top 5% of the distribution, that proportion is found to be the area falling above 2.996 $\theta$. (This value can be easily determined with a hand calculator by entering .05 and pressing the lnX button.)

Step #4

The final step is to multiply the value resulting from step #2 times the value resulting from step #3. In the above example, 1.72 is multiplied by 2.996 which yields 5.15. Therefore, 5.15 times X produces the point above which we have 90% confidence no more than 5% of the measurements fall.