Summary report

Dustiness and particle size testing of copper and copper compounds

EBRC Consulting GmbH Hannover, 20.11.2004 (Dr. R. V. Battersby)

Issue: Assessment of dustiness and particle size distributions of copper compounds and

copper powder with a perspective to the composition of workplace aerosols

Samples: No. 1: copper (I) oxide

No. 2: copper (II) oxide

No. 3: copper (II) sulphate pentahydrateNo. 4: dicopper chloride trihydroxide

No. 5: copper powder

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1. Introduction

Five different copper compounds were subjected to total particle size analysis, with the aim of initially deriving a characteristic d50 value. However, it is well-known that such particle size distributions do not necessarily reflect the particle size of aerosols that may be formed under practically relevant workplace conditions, for example during manual operations such as bag filling and emptying, or under mechanical agitation as in mixing and weighing operations.

For this reason, the particle size distribution of the airborne fraction generated during mechanical agitation in the rotating drum method acc. to Heubach was determined.

Such particle size distribution data has previously been shown to be useful in selecting data sets of analogous substances, but also in predicting particle-size dependant deposition behaviour in the respiratory tract (Battersby & Boreiko, 2004).

The Heubach method also provides a "total dustiness" indicating the propensity of a material to become airborne, and thus serving as an indicator of the mobility under workplace conditions that may be utilised in selecting suitable analogies to other chemical substances with respect to their dermal loading. This approach has been used successfully in the EU risk assessment of Zinc and Zinc compounds, for example.

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2. Methods - Dustiness testing

In dustiness tests with the Heubach-Method, the test material is introduced into a rotating drum apparatus, a test design intended to simulate mechanical stress under conditions of industrial processes involving handling/manipulation of these materials. Any dust thus generated is conveyed in a stream of air to a collection chamber, where it is precipitated and determined gravimetrically. The test result is expressed in "mg/g" of dust/sample. However, in the <u>modified</u> Heubach-Method (acc. to DMT), the generated dust is not collected as a "bulk" sample, but in fact separated in a cascade impactor, which allows a discrimination of the generated dust particles according to particle sizes. The particle size distribution can be recalculated from the aerodynamic diameter (d_a, i.e. the cut off points of the impactor stages) to the physical particle diameter d_p with the following formula, by correcting for the particle density ρ_p (Willeke, 1993):

$$d_{p} = \frac{d_{a}}{\sqrt{\rho_{p}}}$$

3. Methods - Total particle size testing

The total particle size distribution measurements involved a dry dispersion technique with laser-diffraction measurement, in accordance with the following guidelines:

OECD 110: Particle Size Distribution,

CIPAC MT 187: Particle Size Analysis by Laser Diffraction,

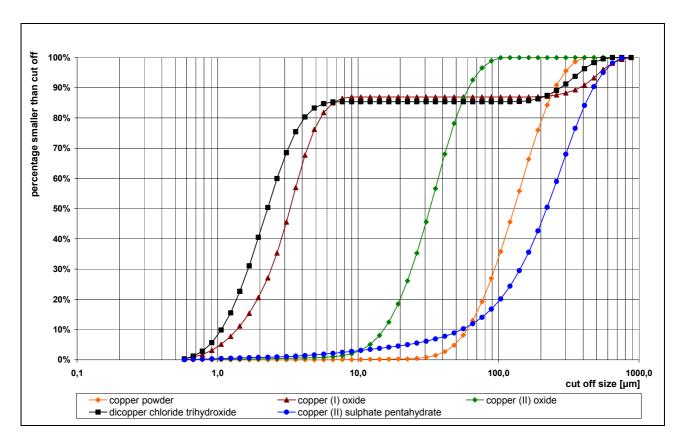
ISO13320-1: Particle Size Analysis - Laser Diffraction Methods.

The test procedure and underlying principles can briefly be described as follows:

- coarse particles are separated from fines by sieving at a mesh size 125 µm, where required.
- the particle size distribution of the fines is determined by laser diffraction. The particles are introduced to the analyser beam by a dry powder feeder by direct spraying into the measurement chamber. The particle size distribution is derived from the recorded diffraction pattern.
- the test item is fed to the dry powder feeder, loosened by an integrated vibrator. The particles are then dispersed and fed to the optical system by pressurised air at 2.5 bar_{abs}, and after passing the spectrometer the sample is collected in a cyclone.
- the average of two measurements is reported as the final result.

4. Results - Total particle size of copper test materials

The particle size distribution as determined by the method described in subchapter 3 above for each batch of test material that was also used in the dustiness testing is presented in the following graph:



Both Copper oxychloride and Copper (i) oxide show a "biphasic" distribution, with a small portion of aggregates with a d50 in the range of approx. 500 µm. The most likely explanation for this is that both of these substances were tested as a technical grade in which they are placed on the market, and as such are stabilised to a level of approx. 0.5% with additives/stabilisers (confidential). The adhesive property of these auxiliary agents is likely to be responsible for this small portion of aggregates.

The other three materials show a very small portion (< 5%) of material with particle sizes of 10 microns or below, indicating by conventional thinking that inhalation exposure during handling of these should be low.

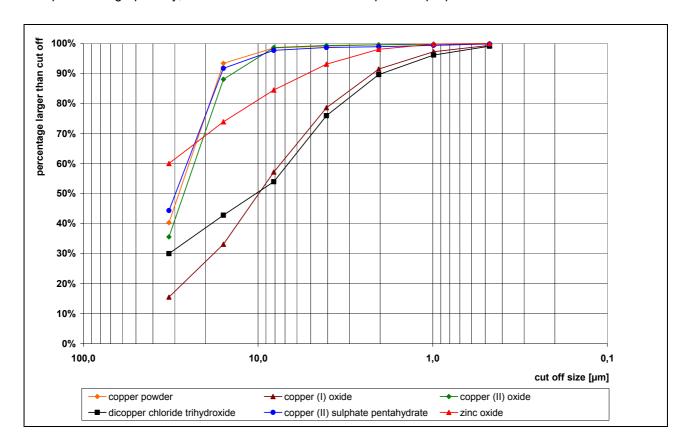
5. Results - Dustiness and particle size distributions of dust generated in the Heubach Dust meter

Both total dustiness and particle size of the fraction of material (determined according to the method described under subchapter 2) that becomes airborne under the conditions of this test is given in the table below. Data for zinc oxide is given for comparative purposes.

	cumulative particle size distribution (%age larger than cut off)					
cut off [µm]	Copper (I) oxide ⁽¹⁾	Copper (II) oxide ⁽¹⁾	Copper (II) sulphate pentahydrate ⁽¹⁾	Dicopper chloride trihydroxide ⁽¹⁾	Copper powder ⁽¹⁾	Zinc oxide ⁽²⁾
0.473	99.38	99.95	99.86	99.13	99.97	99.96
0.989	97.27	99.78	99.40	96.18	99.87	99.84
2.04	91.49	99.57	98.93	89.66	99.61	98.10
4.06	78.63	99.35	98.70	75.99	99.16	93.14
8.13	57.21	98.65	97.74	53.98	98.56	84.53
15.8	33.12	88.11	91.74	42.81	93.42	73.92
32.4	15.52	35.59	44.35	30.00	40.32	60.02
total dustiness [mg/g]	7.07	363.71	48.75	33.36	47.57	30.06

Sources: (1) Selck, 2004; (2) Armbruster, 2000

Based on the raw data from the original reports on dustiness/PSD, the following cumulative distribution is also presented graphically, with zinc oxide included for comparative purposes.



6. Summary of results and conclusions

The data on particle size, dustiness and relative density in comparison to zinc oxide have been summarised in the table below:

Compound	Copper (I) oxide	Copper (II) oxide	Copper (II) sulphate pentahydrate	Dicopper chloride trioxide	Copper powder	Zinc oxide
rel. density ⁽¹⁾ [g/cm³]	5.87	6.32	2.29	3.64	8.9	5.6 ⁽²⁾
d50 ⁽³⁾ [µm]	3.3	32.5	220.4	2.3	129.0	~1 ⁽⁴⁾
total dustiness ⁽⁵⁾ [mg/g]	7.07	363.71	48.75	33.36	45.57	30.1 ⁽⁶⁾

Sources: (1) producer data; (2) Zinc RAR; (3) Franke, 2004a-e; (4) lead company data; (5) Selck, 2004; (6) Armbruster, 2000

Despite the fact that the use of dustiness and particle size distribution data in the assessment of occupational inhalation exposure is far from standardised, use of these parameters has previously been made in the EU Risk Assessment Reports on Zinc and Zinc compounds for the purpose of extrapolation between compounds. Using the same approach, the following tentative conclusions may be drawn with reference to the possibility of extrapolating from occupational exposure data collected for zinc oxide:

- dermal exposure: Copper sulphate, Copper oxychloride, Copper (I) oxide and Copper powder have total dustiness values of a similar order of magnitude as zinc oxide. Given that the perception of potential health hazards for both metals are similar, then it would appear reasonable to extrapolate from zinc oxide to these for the assessment of dermal exposure during handling of finished products. In contrast, since the dustiness of Copper (II) oxide is an order of magnitude higher, extrapolation from zinc oxide could be considered as somewhat limited, and may represent an underestimate.
- inhalation exposure: by comparison of the particle size distributions (previous page), the material that becomes airborne during mechanical agitation of Copper sulphate, Copper (II) Oxide and Copper powder is of a particle size that indicates a low level of respirable particles, in contrast to Copper (I) oxide and Copper oxychloride. In comparison to Zinc oxide, the latter two compounds also do not appear to display the same tendency to aggregate as seen for zinc oxide.

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7. References

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