Fragrance Generic Scenario

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Dilema: # use sites (ie. laundry detergent formulators) can be unreasonably large when calculated from the following equations...

1. From fragrance scenario: **PV/[18-100 kg PMN/site-yr * (250 day/yr/#day/yr) * (0.5%/PMN conc.)]**

(basis: amt PMN used/site-yr is EPA (1973) model small soap and liquid detergent plant capacity and minimum PMN conc. in final product of 0.001% assumed)

2. Propose this eqn.: **PV/(detergent kg/site-yr * %PMN in detergent)**

Detergent capacity (kg/site-yr)

1.8e6 - 1.1e7 EPA (1973) model small soap and liquid detergent plant capacity (fragr. scen.)

6.4e6 BOC 1995, powder detergent mfg 1992 (surf. scen.)

1.2e7 BOC 1995, liquid detergent mfg 1992 (surf. scen.)

4.5e6 - 2.7e8 "Economic Analysis of Proposed Effluent Guidelines for Soap and Detergent Industry" 8/73, EPA 1983, small - large powder detergent plants (surf. scen.)

1.1e7 - 2.3e7 "Economic Analysis of Proposed Effluent Guidelines for Soap and Detergent Industry" 8/73, EPA 1983, small - large liquid detergent plants (surf. scen.)

PMN concentration in final product (%)

0.001 - 1 Umbach 1991, soaps and detergents (fragr. scen.)

Result when plugged into eqn. 2:

PV/[(106 - 108 kg/site-yr) * (10-3 - 100 % PMN)]-->denominator spans 6 orders of magnitude

Options:

a. large # of small sites (lg # workers) --> **PV/(10e3 - 10e6) depending on %PMN**

b. small # of large sites (sm # workers) --> **PV/(105 - 10e8) depending on %PMN**

worst case occupational exposure = option "a" with max %PMN = **PV/(106)**

worst case environmental release = option "b" with max %PMN = **PV/(108)**

Questions:

1. Which option should we pick if either?
2. Can we narrow the detergent production capacity and/or %PMN ranges? - get info from detergent trade association? PMN submissions search?
3. Can we find a meaningful mean? -take log of each endpoint, calc mean, return to normal
4. Should we use detergent production capacity default given in surfactant scenario? - 6e6 for powder (60%market share), 1e7 for liquid(40% market share) -> 9e6 ->1e7 kg/site-yr

MANUFACTURE AND USE OF FRAGRANCES

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Prepared for the Chemical Engineering Branch by SAIC

MANUFACTURE

Market Profile:

Fragrance or aroma chemical manufacture is a small and specialized branch of the organic specialty chemical industry. Like other organic chemicals, the products are usually made in batches using relatively simple processes. However, the fragrance industry requires raw materials that are free of impurities (these would affect the aroma) and produces very small volumes of product on an annual basis. Of the approximately 3,000 aroma chemicals used in blending or compounding fragrances (Grant, 1985):

- 88% are used in quantities less than 1 mton/yr, with many less than 0.1 mton/yr
- 8.3% are used in quantities from 1 to 10 mton/yr
- 2% are used in quantities from 10 to 100 mton/yr
- 1.3% are used in quantities from 100 to 1,000 mton/yr
- 0.7% are used in quantities greater than 1,000 mton/yr.

In 1980, approximately 79,000 mton of aroma chemicals were produced by 42 companies (Frost and Sullivan, 1982). However, estimating production volumes is difficult due to a lack of universal definitions and complex formulations.

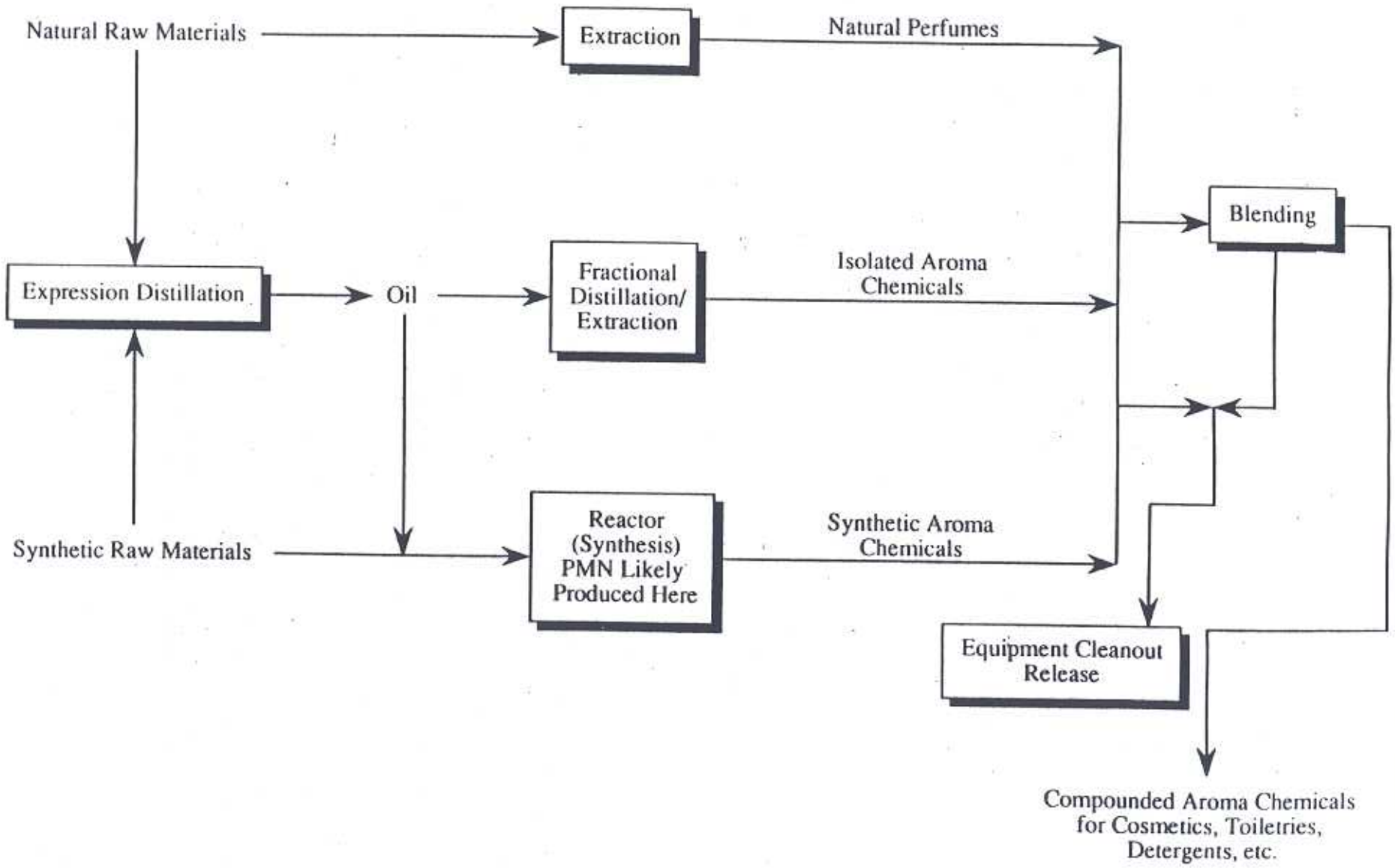
Since the 1960s, sources of materials used in the fragrance industry have shifted from natural to synthetic, due to laws protecting animals, advances in chemistry, and cost advantages. In 1984, 85% of materials used were synthetic (Grant, 1985).

Process Description:

Fragrance manufacture and formulation is a batch process. Review of available information indicates that a single site will typically manufacture a specific aroma compound, store it, and formulate it with other substances for sale. Therefore, a separate evaluation for fragrance formulation will typically not be necessary. A single fragrance formulation may contain from 20 to several hundred individual aroma chemicals (Givaudan-Roure, 1992).

The natural raw materials are derived from animals or plants. The essential oils are drawn from the plant material (e.g., fruits, flowers, branches) by crushing, steam extraction, or alcohol extraction. A process flow diagram of aroma chemical manufacturing is attached; additional information may be supplied by the PMN submitter.

Process Flow Digram for the Manufacture of Aroma Chemicals



The various components are compounded (blended) by mixing together in a vat. Crystals are added first, followed by other materials in order of decreasing viscosity. Mixing requires several hours and heat is avoided to preserve highly volatile and sensitive components. The fragrance can then be filtered (Kirk-Othmer, 1980). The material is then packaged and sold.

Number of Manufacturing Sites: Given.

Days of Operation: Given or assume 250 days per year.

Worker Exposure: Given or assume 6 to 12 workers per site (Givaudan-Roure, 1992). Tasks include chemical handling and addition to blend tank, transfer from tank to packaging, filter change-out, and equipment cleanout and maintenance.

A. Inhalation

1. If PMN is in a solid state prior to formulation, use the OSHA PEL for dust in CEB's standard model:

$$I = C_m bh$$

where: I = Daily inhalation exposure, mg/day
C_m = Airborne concentration of PMN, mg/m^3
b = Inhalation rate, m/hr
h = duration, hr/day

I= 150 mg/day = 15 mg/m^3 x 1.25 m^3/hr x 8-hr TWA exposure for initial chemical handling

2. If PMN is in a liquid state prior to formulation, exposure may be negligible due to low vapor pressure. However, perfumes exist to be smelt. They are also intended to be persistent but not overpowering. These factors tend to result in fragrance chemicals with moderate vapor pressures, around 0.05-10 mmHg. *d*-Limonene, the essential oil of lemons which is commonly added to household bleach, has an estimated vapor pressure around 2.1 mmHg. NIOSH has reported on occupational exposure to vapors during perfume manufacture (NIOSH, 1992). The perfume being manufactured at that site consisted, as most perfumes do, primarily of ethanol. The observed 8-hour TWA airborne concentration of ethanol (vapor pressure 57 mmHg) was 45-53 ppm. If the mole fraction of the PMN chemical in the perfume is known, then the airborne concentration can be estimated by the "analogous chemical" method to be:

$$C_v = 50\left(\frac{Px_1}{57}\right)$$

where

C_v	=	Concentration of PMN chemical in air, ppm
P	=	Vapor pressure of PMN chemical, mmHg
x_i	=	Mole fraction of PMN in the perfume

This equation applies even if the base solvent for the perfume is not ethanol. It should be used with some caution, as it is based on limited data. The airborne concentration of *d*-limonene in the same plant was 0.16-0.28 ppm. Since the concentration of *d*-limonene in the perfume was not reported by NIOSH, this cannot be used for quantitative calculations but may be useful as a comparison.

B. Dermal

Assume 3,900 mg/day from routine 2-hand contact of the pure substance (prior to blending).

Environmental Release:

A. Air

The perfume plant described above had a ventilation rate of 4,000 cubic feet per minute, giving an ethanol loss rate of 5.1 kg/day. These losses arose from container filling operations, and should therefore be proportional to MP, where M is the molecular weight and P is the vapor pressure. The following expression provides an estimate of the loss rate of PMN:

$$Q_a = 5.1 \times \left(\frac{M_i P_i x_i}{(46.07)(57)} \right)$$

where

Q_a	=	Mass flux to atmosphere, kg/site-day
M_i	=	Molecular weight of PMN chemical
P_i	=	Vapor pressure of PMN chemical, mmHg
x_i	=	Mole fraction of PMN chemical in perfume

B. Water

Releases to water will consist of equipment cleanout only.

C. Land

Releases to land are not expected from fragrance manufacture.

USE

Market Profile:

Fragrances are used in the following applications:

End Use	Market Share[1]	% Perfume Oil in Product[2]	Total # of Sites[3]
Cosmetics and toiletries	34	0.2-3.0	694 (SIC 2844)
Soaps and detergents	27	0.8-2.0	764 (SIC 2841)
Perfumes and colognes	19	3-30	(included in SIC 2844)
Other	20	Not available	Not available
Total	100	0.2-30	1,458

1. Frost and Sullivan, 1982.
2. Umbach, 1991.
3. 1987 Census of Manufactures, U.S. Department of Commerce.

"Other" uses may include fumigants, perfumed candles, printing ink, and paint (Billot, 1975).

Because perfume oil is a blend of 20 to hundreds of different aroma chemicals, the concentration of a PMN chemical in a perfume oil formulation (i.e., as received by the user) is expected to be on the order of 0.5 to 5 percent, with a PMN chemical concentration in the end product on the order of 0.001 to 1 percent.

It should be noted that a significant portion of the production of flavor and perfume chemicals is used in foods and the cosmetic and toiletry industry. These end-uses are not regulated by TSCA.

Process Description:

This scenario considers the use of fragrances in mixing and packaging detergents, cosmetics, etc. It does not include subsequent use of these products by the service industry (e.g., janitorial), which would likely result in thousands of workers at hundreds of sites being exposed to low concentrations of the PMN.

Unless additional information is given, it is assumed that the PMN substance is used in all of the end uses presented above. The following process description is applicable for the three end uses named above: cosmetics and toiletries, soaps and detergents, and perfumes and colognes.

The fragrance is transferred from shipping containers into storage bins or tanks, then added to the soap or other base material by mixing. The material is then packaged. Powdered soap and detergent has an additional step of spray drying prior to packaging (AP-42, 1988), while other soap goes through additional steps of extrusion, cutting, and molding prior to packaging (Umbach, 1991). Processing may be a continuous or batch operation depending on the product and scale of operation.

Number of Use Sites:

Sites = PV / (18 to 100 kg) x (250 days/# days/yr) x (0.5%/PMN Concentration)

Days of Operation: Assume 250 days/yr of operation if not given.

Assume PMN concentration of 0.5% if not given.

Basis: Accounting for soap and detergent use only, a small site will consume a minimum of approximately 18 to 100 kg PMN substance/yr (assuming 250 days of operation). This is based on an EPA (1973) model small soap plant with a capacity of 4 million pounds/yr and a model small liquid detergent plant with a capacity of 25 million pounds/yr, and a minimum PMN concentration of 0.001 percent in the final product (see "Market Profile"). Typical plant sizes for other industries using fragrances are not available; it is assumed that these plants will use the PMN at a similar rate.

Worker Exposure: Assume 6-12 (Number of workers is not expected to be more than those potentially exposed during manufacturing).

The number of workers potentially exposed to powdered soap dust (see Inhalation scenario below) is expected to be approximately 10 percent of the total number of workers. This is based on the market share of fragrances used in soap (27 percent, from Frost and Sullivan, 1982) and the value of powdered soap produced as compared to all soap (30 percent, from DoC, 1987).

A. Inhalation

Inhalation estimates will vary depending on the physical state of the fragrance formulation and the end use. If the physical state of the PMN is not given, assume liquid. (Billot (1975) provides formulation information for several fragrances; in all cases, these are formulated with water or alcohol in a liquid state.) If the PMN end use is not specific, assume it will be used for powdered soap manufacture and exposure to product dust may result.

1. If PMN is in a solid state leaving the manufacturing site or is used for powdered soap manufacture, there is a potential for dust inhalation. NIOSH has measured detergent dust concentrations in the air at two manufacturing plants. The following results were obtained:

obtained:

Site	Particle concentration, $mg.m^{-3}$		% < 10 μm
	Median	Range	
Clorox (NIOSH 1980, 45 samples)	0.52	0.19-3.71	76
Purex (NIOSH 1978, 25 samples)	3.26	1.1-18.9	14
Respirable particles, both sites	0.38	0.14-2.82	

If the PMN is in a solid state leaving the manufacturing site and the concentration is not given, assume 0.5 to 5 percent. If powdered soap end use is being evaluated and the concentration is not given, assume 0.004 to 0.1 percent.

2. If PMN is in a liquid state leaving the manufacturing site, use the CEB Manual if the vapor pressure is significant. Worker activities include product transfer, packaging, and sampling. Therefore, Tables 4-11 (for packaging) and 4-12 (for sampling) in the Manual may be appropriate.

B. Dermal

Assume 3,900 mg/day x PMN Concentration, from routine 2-hand contact of the perfume oil prior to incorporation into the final product. If the concentration leaving the manufacturing plant is not known, assume 0.5 to 5 percent.

Environmental Release:

A. Air

If it is appropriate to assume the fragrance may be incorporated into powdered soap, use total air releases of dust at 0.7 percent of the use volume (AP-42, 1988). Use the previously calculated number of sites and number of days to calculate air releases on a kg/site-day basis.

B. Water

Water releases should be limited to equipment cleanout.

C. Land

Releases to land should be limited to container residue.

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