Use of Additives in Papermaking- Generic Scenario for Estimating Occupational Exposures and Environmental Releases

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Scope of Scenario:

The papermaking process includes the following steps: *stock preparation* for papermaking, paper manufacture *wet end operations*, and paper manufacture *dry end operations*. This scenario presents methods that can be used to estimate releases and exposures to the following papermaking additives: acids and bases, alum, sizing agents, dry-strength adhesives, wet-strength resins, fillers, coloring materials, retention aids, flocculants, defoamers, drainage aids, optical brighteners, pitch control chemicals, slimicides, and specialty chemicals. The generic scenario is applicable to chemicals that are used during the stock preparation step or as on-machine additives in the papermaking process. The scenario covers the introduction of the additive to the papermaking process through to the final disposition of the additive either in the paper product or as waste.

Converting operations that occur off of the paper machine and the manufacture of the paper additives are beyond the scope of this scenario and are not addressed in this document. This scope could be narrowed to cover only additives in papermaking operations involving pulped fiber as the stock; however, the wet end of the paper machine is similar for most grades of paper.

Industry Sector Description:

Pulp and paper mills in the U.S. can be divided into three major categories: mills that produce pulp only (market pulp facilities), mills that only manufacture paper from pulp (non-integrated facilities), and mills that produce both the pulp and the paper on site (integrated facilities).

According to the U.S. Census Bureau's County Business Patterns (CBP) for 2001, a total of 555 establishments were classified in North American Industry Classification System (NAICS) codes 32212 and 32213. These cover the paper and paperboard manufacturing industry sectors and include both integrated and non-integrated papermaking facilities. Table 1 shows the distribution of establishments based on the total number of workers at each establishment:

Table 1
Number of Establishments by Employment-Size Class for the Paper and Paperboard Manufacturing Industry Sectors
(NAICS Codes 32212 and 32213)

	Number of Employees									Total Establishments
	1-4	5-9	10-19	20-49	50-99	100-249	250-499	500-999	≥1000	
Number of Establishments	43	19	18	35	116	130	85	74	35	555

Over 80% of all facilities employ a total of 50 or more workers.

Table 2 presents paper and paperboard production for 2001 and 2002:

Table 2
U.S. Paper and Board Production in (1,000 tons/year)

Product	2001 (short ton)	2001 (metric ton)[1]	2002 (short ton) [2]	2002 (metric ton)[1] (PV_{pro})
Paper (total)	42,266	38,344	41,479	37,630
Tissue	7,013	6,362	7,107	6,447
Newsprint	6,442	5,844	5,785	5,248
Packaging and Paperboard (total)	46,822	42,477	47,745	43,314
Total	89,088	80,821	89,224	80,944

[1] Calculated from value in short ton from source using conversion of 0.9072 metric ton/short ton.
[2] Value for Paper (total) estimated by estimating an equal amount of uncoated groundwood shipments in December as November. The December amount of uncoated groundwood shipments is listed in the source as not available.

Sources:

U.S. Census. County Business Patterns. U.S. Census Bureau. *http://censtats.census.gov/cgi-bin/cbpnaic/sel.pl* Downloaded September 23, 2003.

"Month in Statistics" Pulp & Paper, April 2002, Vol. 76 Number 4, pg. 15; April 2003, Vol. 77 Number 4, pg. 11.

Process Description:

The papermaking process includes the following steps: *stock preparation* for papermaking, paper manufacture *wet end operations*, and paper manufacture *dry end operations*.

Stock Preparation

Stock preparation is the interface between the pulp mill or pulp warehouse and the paper machine. In an integrated mill, stock preparation begins with dilution of heavy stock at the discharge of high-density pulp storage chests and ends with blended papermaking furnish in the machine chest. The *furnish* is the mixture of various materials that are blended into a stock suspension from which paper or board is made. At a non-integrated mill, stock preparation begins by feeding pulp bales into the repulping system and, again, ends with the blended papermaking furnish in the machine chest.

Stock preparation takes the required raw materials (pulps) and non-fibrous ingredients (additives), treats and modifies each furnish as required, and then combines all ingredients continuously and uniformly into the papermaking stock. Uniform papermaking furnish is the key to ensuring stable paper machine operation and a high standard of paper quality. A typical fiber concentration for furnished stock is about 3%. The following operations are common to stock preparation:

- **Pulping:** Baled pulp or other fibrous raw material is dispersed into water to form a slush or slurry. This operation may be either batch or continuous.

- **Refining (or beating):** Fibers are subjected to mechanical action to develop their papermaking properties based on the product to be made. This operation is usually continuous.

- **Addition of Wet End Additives:** A variety of mineral and chemical agents are added to the stock to give specific properties to the paper product or to facilitate the papermaking process.

- **Metering and Blending:** Various fibrous and nonfibrous components are continuously combined and blended to form the papermaking stock.

Wet End Operations

The paper machine is a device used to continuously form, dewater, press, and dry a web of paper fibers. The most common types of wet end machines are the *fourdrinier* and *twin wire* formers. The furnish (i.e., fiber suspension) formed in the stock preparation step is fed to the former. Water is removed from the fiber suspension by gravity or a pressure differential developed by table rolls, foils, or suction equipment. More water is then squeezed out in the press section of the former. Finally, the sheet is dried with steam heating in the dryer section of the former.

Twin wire formers are machines that use two wires to form and drain water from the dilute pulp slurry. These machines apply a jet of stock onto two converging wires to speed up water removal and maintain better web uniformity.

Typical consistencies for wet end operations are 0.3 to 0.6%. In wet end operations, chemicals may be added into the paper machine approach system and at the paper machine headbox (described below).

The wet end operations on the paper machine include the following sections and systems:

- **Approach System** - The fan pump loop is where the papermaking furnish is metered, diluted, mixed with any necessary additives, and screened and cleaned before being discharged onto the paper machine forming medium in the sheet-forming section (see below). The approach system extends from the storage chest to the headbox. The fan pump mixes the stock with white water and delivers the blend to the headbox.

- **Headbox** - The headbox takes the stock delivered by the approach system fan pump and transforms the pipeline flow into an even, rectangular discharge equal in width to the paper machine and at uniform velocity in the machine direction (i.e., the direction of paper parallel with the direction of movement on the paper machine). Additives may also be incorporated into the stock at the headbox.

- **Sheet-Forming Section** - The *forming medium* is an endless, finely woven belt (usually made of plastic mesh fabrics) that travels between two large rolls: the breast roll (near the headbox) and the couch roll (at the other end of the forming section). The various elements between these two rolls serve to support the wire and as water removal mechanisms. Most machines use a forming board immediately after the breast rolls followed by a number of foil assemblies. The wire then passes over a series of vacuum devices (from low vacuum to high vacuum) and finally over the high-vacuum couch roll. Water drained by hydraulic pressure gradients from the sheet enters the white water recirculation system. In twin wire forming, the water drainage can take place in one direction or in both directions. The dewatering action is due to pressure set up by the tension in the two wires and by water drainage elements outside of the wires.

- **Pressing** - The pressing section removes water from the sheet and consolidates the paper web. In the pressing section of the paper machine, the paper web is transferred from the forming section and conveyed on specially constructed felts through a series of roll press nips and into the dryer section. The pressing operation is an extension of the water removal process started in the sheet forming section. In addition, the sheet consolidation that occurs during this operation forces the fibers into intimate contact with one another so that fiber-to-fiber bonding can occur.

- **Vacuum System** - Vacuum-assisted drainage elements of the paper machine include suction boxes in the forming section and vacuum rolls in both the sheet-forming and press sections. Several types of vacuum systems are used; the most common employs positive-displacement, liquid ring vacuum pumps.

- **Broke System** - Broke, which can be wet or dry, is the partially or completely manufactured paper or paperboard that is discarded at any point in the paper manufacturing or finishing process. The term also applies to the furnish made by repulping these materials. Wet broke is taken from the forming and pressing sections, while dry broke is taken from the dryers, calenders, reel, winder, and finishing operations. Wet broke is fairly simple to repulp because the sheet disintegrates easily and does not need to stay in the repulping system long. Repulping is accomplished using various types of agitators and extraction generally performed through a perforated plate. As necessary, the slurry is transferred to storage and reintroduced through the blending system into the machine furnish. Dry broke is treated similarly; however, heavier-duty agitation and deflaking equipment is used and retention time in the repulping unit is greater.

- **White Water System** - White water is the drainage from the wet end operations. White water contains fiber and may contain a variety of other furnish-derived materials. White water is classified as either *rich* or *lean* depending on the fiber content. The white water is richest in the area where the headbox jet impinges on the wire and becomes progressively leaner as a fiber mat builds up on the forming medium.

  The rich white waters are collected in the wire pit and immediately recirculated in the approach loop. Leaner white water is used as make up in the wire pit or dilution in the stock preparation area. Only the leanest water is removed from the system and pumped to on-site water treatment prior to discharge. The reusable fibers and fillers in paper machine white water overflow streams are reclaimed into the machine furnish, typically via flotation savealls and disc filters. Clarified white water is used for wire and felt showers, press section waters, vacuum system waters, and cooling water.

<u>Dry End Operations</u>

Dry end papermaking operations include paper drying, calendering, reeling, winding, and roll finishing. In dry end operations, chemicals may be added to the papersheet during the drying and calendering operations.

Dry end operations on the paper machine include the following:

- **Paper Drying** - After pressing, the paper sheet (containing 55-60% moisture by weight) is conveyed through the dryer section where the residual water is removed by evaporation. The sheet passes over a series of rotating steam-heated cylinders where the water is evaporated and carried away by ventilation air. The paper web is held tightly against the cylinders by a synthetic permeable fabric (the dryer felt). The fabric supports and guides the paper sheet through the dryer section, helps to keep the sheet flat, and in some cases may help in control cross-direction shrinkage. The heat energy for paper drying is generated by steam as it condenses inside the dryer cylinders. The condensate that forms in the dryer cylinders is removed by a siphon assembly. Other methods of paper drying include *air-impingement* and *infrared* drying for coatings where contact with a steam cylinder would cause adhesion problems; *air-borne* drying for extensible papers; and *air-through* drying for lightweight porous papers such as tissues.

- **Surface Sizing** - Sizing operations are performed to make the paper resistant to aqueous solutions. In surface sizing, a sizing solution is commonly applied on the paper machine at a station between dryer sections. The sizing is applied within a two-roll nip, which is referred to as a *sizing press*. For heavier paper and boards, surface sizing is commonly applied at the calender stack using a water box and a rubber lip that contacts the calender roll.

- **Coating Operations** - Many types of papers are coated with pigment-rich formulations to provide improved gloss, smoothness, color, opacity, printing quality, and brilliance. The coating can be applied on the paper machine (i.e., "on-machine") or "off-machine". On-machine coatings are applied in a method similar to a size press. Coating processes are categorized as either pigment coating or functional coating. Most on-machine coating is pigment coating, while functional coating with lacquer, varnish, waxes, or resins is usually done off-machine as part of converting operations (not covered in this scenario). Mineral pigments used in coatings are similar to fillers. They are mixed with adhesives and other components to bind to the paper surface and to provide suitable finish and rub-resistance. After drying and calendering, the coating provides a smooth, even surface for printing.

- **Calendering** - Most paper grades are calendered (i.e., pressed with a roll) to obtain a smooth surface for printing. Calendering also improves the cross-direction thickness uniformity, which is important for reel-building and converting.

- **Reeling** - Reeling is the process of rolling the paper product onto a drum reel for subsequent processing off of the paper machine.

- **Winding** - In the winding operation, the large-diameter paper reel is cut and wound into suitable-size rolls. These rolls may then be wrapped and sent directly to the customer or they may be processed through subsequent coating, calendering, sheeting operations or rewinding.

- **Roll Finishing** - The steps in roll finishing include scaling, wrapping, crimping (where the wrapper overlap is folded over), heading (where a circular piece of wrapping is glued over the crimped overlap), and labeling.

<u>Addition of Additives in Papermaking</u>

Table 3 lists the types of chemical additives that may be added in papermaking. Papermaking additives can be introduced at various stages of the papermaking process. In stock preparation, additives are blended with the stock in the machine chest. The additives commonly used include alum, sizing agents (both internal and surface), mineral fillers, starches, and dyes. Chemicals for control purposes such as drainage aids, defoamers, retention aids, pitch dispersants, slimicides, and corrosion inhibitors are added as required.

In wet end operations, additives are mainly introduced in the approach system of the paper machine. Internal sizing is commonly added at the wet end operations.

Surface sizing solution is often applied to the dried sheet at a later stage in the process (i.e., dry end operations). The pigment coatings may also be applied in the dry end operations.

Note: the information presented in Table 3 should only be used in the absence of chemical-specific information.

Sources:

Smook, G.A. Handbook for Pulp and Paper Technologists 2nd Edition. 1992.

European Commission, "Integrated pollution prevention and control (IPPC) - draft reference document on best available techniques in the pulp and paper industry," August 1999.

Table 3
Paper Machine Additives and Their Application

Additive	Application	Application Rate (lb/t of paper)[1]	Application Rate (kg/t of paper)[2]
Acids and bases	Control pH	NA	NA
Alum	Control pH; fix additives onto fibers; improve retention	NA	NA
Sizing agents	Control penetration of liquids into paper surface	NA	6.4
Dry-strength adhesives	Improve burst and tensile strength; add stiffness and pick resistance	NA	NA
Wet-strength resins	Add wet strength to toweling and wrapping grades	NA	NA
Fillers	Improve optical and surface properties	NA	209.3
Coloring materials	Impart desired color	NA	NA
Retention aids	Improve retention of fines and fillers	NA	NA
Flocculants	Improve sheet formation	NA	NA
Defoamers	Improve drainage and sheet formation	NA	NA
Drainage aids	Increase water removal on the paper machine wire	NA	NA
Optical brighteners	Improve apparent brightness	NA	NA
Pitch control chemicals	Prevent the deposit/accumulation of pitch	NA	NA
Slimicides	Control slime growth	NA	NA
Specialty chemicals	Such as corrosion inhibitors, flame proofing and antitarnish chemicals	NA	NA
Other additives and dyes	The application rate was given for this grouping of additives. Refer to the specific additive for application.	NA	15.4

NA - Not available
[1] Additional information on typical application rates for specific additives is being researched. We expect the information we find to be in the form of lb/t, which would then be converted to kg/t for use in the scenario.
[2] The information presented was found in the initial data search performed for this scenario.

Process Flow Diagrams:

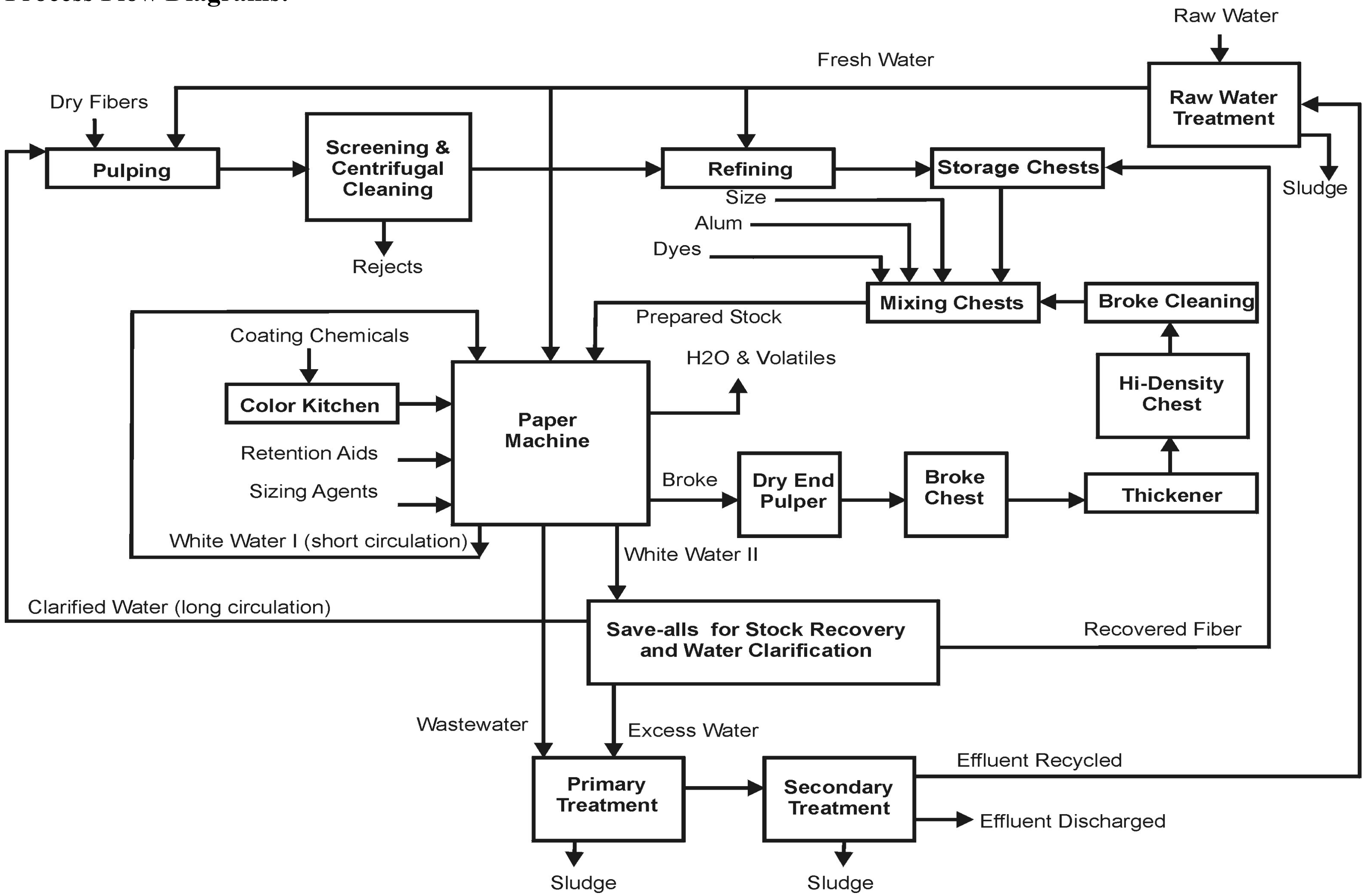


Figure 1. Standard Process for Non-integrated Paper Mills (Source: Crechem Technologies Inc.)

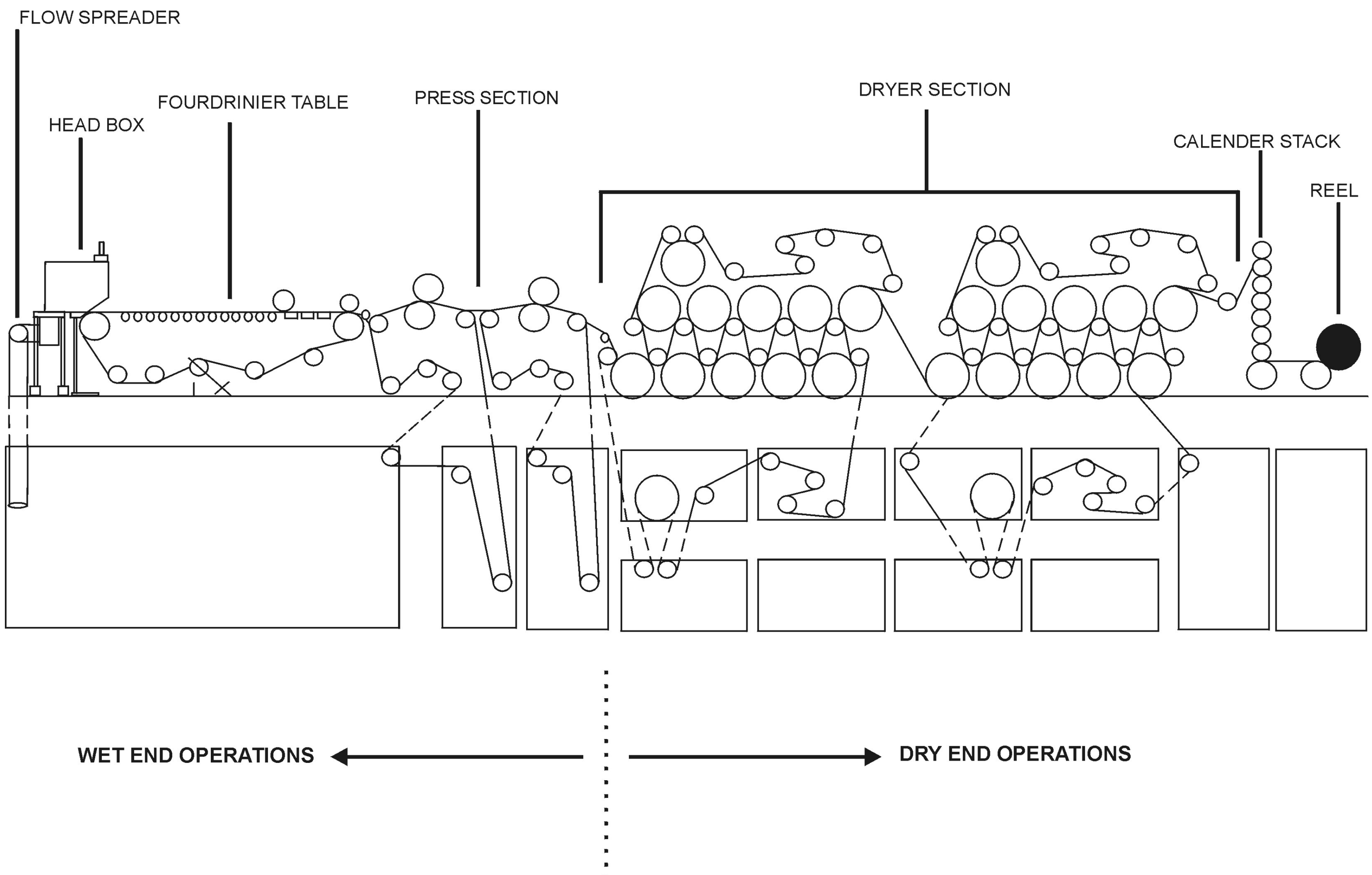
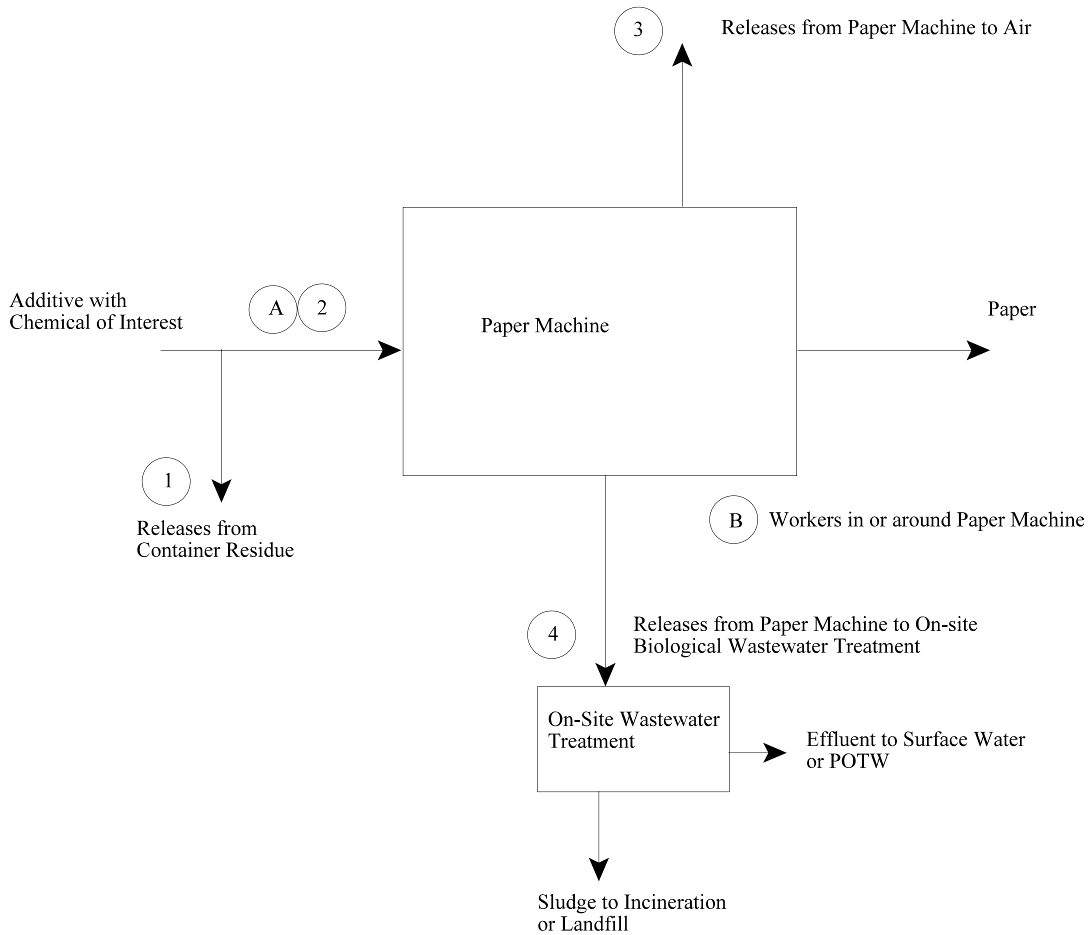


Figure 2. Fourdrinier Style Paper Machine **(Source: EPA/821-R-93-019)**



Releases

$\boxed{1}$ Release to water, incineration, or landfill of container residue

$\boxed{2}$ Release to air from transferring to paper machine

$\boxed{3}$ Release to air from papermaking machine

$\boxed{4}$Release to on-site wastewater treatment from papermaking machine

Exposures

$\boxed{A}$ Dermal and inhalation exposure to the chemical of interest from transferring to paper machine

$\boxed{B}$ Inhalation exposure to mist generated by paper machine

Figure 3. Process Flow Diagram for Releases and Exposures

General Facility Estimates:

Default values cited within this section of the scenario are intended to be used when site-specific information is not available.

I. Operating Days

Paper mills and paperboard mills are expected to operate 350 days per year.

Source:

U.S. EPA. Development Document for Proposed Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard Point Source Category. EPA/821-R-93-019. Washington, DC. October 1993.

II. Daily Paper Production

Using the paper production data, number of total paper mills in the U.S., and typical number of days of operation, industry production estimates can be determined using the following equation:

$$DMO_{pro} = \frac{PV_{pro}}{OD \times TS}$$

Example calculation for daily paper production using default values:
DMO_{pro} = 80,944,000 t/yr / (350 days/yr × 555 sites) = 417 t/site-day

Where:

DMO_{pro}	=	Daily paper production (t/site-day)
PV_{pro}	=	Annual production of paper or board in the U.S. (Default: 80,944,000 metric ton/yr, See Table 2)
OD	=	Number of operating days per year (Default: 350 days/yr)
TS	=	Total number of sites in the U.S. (Default: 555 sites; Alternative defaults: 308 sites for paper mills and 247 sites for paperboard mills)

Using the most current information available on paper and paperboard production and relative number of mills, along with the estimate of 350 operating days per year for this industry, the following industry production estimates can be made:

Table 4

U.S. Paper and Board Production per Site

Product	Ton/Year	Ton/Day	Number of Sites (TS)	Ton/Site-Day (DMO_{pro})
Paper (total)	37,630,000	107,510	308	349
Tissue	6,447,000	18,420	NA	NA
Newsprint	5,248,000	14,990	NA	NA
Packaging and Paperboard (total)	43,314,000	123,750	247	501
Total Papermaking	80,944,000	231,270	555	417

Note: All of these values will give more conservative estimates for exposures than the 1,000 tons per day benchmark proposed.

III. <u>Daily Use Rate</u>

Using the daily paper production rate calculated above, the daily use rate of the chemical of interest can be determined using the following equation:

$$DMO_{chem} = DMO_{pro} \times Y_{chem}$$

Example calculation for daily use rate of chemical of interest using default values:
DMO_{chem} = 417 t/site-day × 15.4 kg/t = 6,422 kg/site-day

Where:

DMO_{chem}	=	Daily use rate of chemical of interest (kg/site-day)
DMO_{pro}	=	Daily paper production (t/site-day)
Y_{chem}	=	Amount of chemical of interest used in papermaking per ton of paper (Default: 15.4 kg/t of paper, see Table 3)

IV. <u>Number of Sites</u>

The number of sites using the chemical of interest can be estimated by using the annual production volume of the chemical of interest, daily use of the chemical of interest and amount of paper produced. The number of sites can be estimated using the following equation:

$$NS = \frac{PV}{DMO_{chem} \times OD}$$

Example calculation for number of sites, using default values and a production volume of 20,000,000 kg/yr:
NS = 20,000,000 kg/yr / (6,422 kg/site-day × 350 day/yr) = 9 sites

Where:

NS	=	Number of sites
PV	=	Production volume of the chemical of interest (kg/yr)
DMO_{chem}	=	Daily use rate of chemical of interest (kg/site-day)
OD	=	Number of operating days per year (Default: 350 days/yr)

The values for daily use rate (DMO_{chem}), number of sites (NS), and production volume of the chemical of interest (PV) are all related. This scenario presents an equation to calculate the parameter for the daily use rate (DMO_{chem}) from average industry data (annual production, total number of sites). The chemical of interest throughput and supplied production volume are used to determine the number of sites.

If the number of sites is known, the chemical of interest throughput (DMO_{chem}) can be calculated directly from the known production volume for the chemical (PV) without the use of the average industry data (DMO_{pro}) by using the following equation:

$$DMO_{chem} = PV/(NS \times OD)$$

Environmental Release Assessments

1. <u>Container Residue (Release 1)</u>

The standard CEB release models will be used to estimate this release. The particular model used will depend on the size of the container and the physical form of the chemical additive when delivered to the paper mill. Papermaking additives can be transported in containers of various sizes ranging from sacks to railcars. The most common containers found for papermaking additives are totes, railcars, and tankcars. These containers are received from the additive formulator or manufacturer and are expected to contain residual after unloading activities. Specific data describing transport container cleaning and waste disposal at papermaking sites have not been found. The media of release for transport container residue is uncertain. Therefore, transport container residue disposal may be released to on-site water treatment, water, incineration or landfill.

To ensure a conservative release estimate when the specific container information is unknown, it is assumed that a liquid chemical additive is received in 55-gallon (208-L) drums as a default. While some mills may utilize dedicated containers for some additives, the scenario will assume that the residues from each container are disposed each time the container is emptied for the most conservative estimate.

The information presented for this standard CEB model is based on the current version of the model (as of the date of this generic scenario). Standard CEB models are subject to change; therefore, the most current version of the standard CEB model should always be used.

The number of containers emptied per site is based on the daily use rate, container size, density of the fluid, and concentration of the chemical of interest in the additive. If the fluid density is not known, a density of 1 kg/L (water) can be used as a default. If the concentration of the chemical of interest in the additive is not known, then the default value for the concentrate should be used. The number of containers can be estimated through the following equation:

$$NSC = \frac{DMO_{chem} \times OD}{Y_{add} \times V_D \times D_{AC}}$$

Example calculation for number of containers:
NSC = 6,422 kg/site-day × 350 day/yr / (1 × 208.2 L/container × 1 kg/L) = 10,796 containers

Where:

NSC	=	Number of shipping containers (containers/site-yr)
DMO_{chem}	=	Daily use rate of chemical of interest (kg/site-day)
OD	=	Number of operating days per year (Default: 350 days/yr)
Y_{add}	=	Weight fraction of chemical of interest in additive component (Default: 1)
V_D	=	Volume of container (Defaults: 55 gal/drum (208.2 L/container))
D_{AC}	=	Density of additive component (Default: 1 kg/L)

The following equation calculates the release of the chemical of interest from the cleaning of one container:

$$CR = V_D \times D_{AC} \times Y_{add} \times LF_{CR}$$

Example calculation for container residue:
CR = 208.2 L/container × 1 kg/L × 1 × 0.03 = 6.25 kg/container

Where:

CR	=	Release of chemical of interest from container cleaning (kg/container)
V_D	=	Volume of container (Default: 55 gal/drum (208.2 L/drum))(9)
D_{AC}	=	Density of additive component (Default: 1 kg/L, assume density similar to water)
Y_{add}	=	Weight fraction of chemical of interest in additive component (Default: 1)
LF_{CR}	=	Loss fraction of chemical of interest that remains in the shipping container as residue (Defaults: 0.03 for drums, liquid; and 0.01 for solids)(9)

If the number of containers (NSC) is <u>less</u> than the number of days of operation (OD), then the frequency of the release is equal to the number of containers.

If the number of containers is <u>greater</u> than the days of operation, the days of release is equal to the days of operation, and the average daily release is calculated based on the following equation:

$$CR = DMO_{chem} \times LF_{CR}$$

Example calculation for container residue:
CR = 6,422 kg/site-day × 0.03 = 193 kg/site-day

Where:

CR	=	Release of chemical of interest from container cleaning (kg/site-day)
DMO_{chem}	=	Daily use rate of chemical of interest (kg/site-day)
LF_{CR}	=	Loss fraction of chemical of interest that remains in the shipping container as residue (Defaults: 0.03 for drums, liquid; and 0.01 for solids)

Sources:

Memorandum: "Revised Compilation of Guidance Memoranda (1992 - May 1999);" from Kurt Rindfusz, ERG to Nhan Nguyen, CEB Engineers, ERG PMN Team; December 2, 1999.

Resource Conservation and Recovery Act 40 CFR Chapter 1 Part 261, RCRA Online. http://www.access.gpo.gov/nara/cfr/waisidx_02/40cfr261_02.html (last confirmed June 2003)

PEI Associates, Inc. 1986. Releases During Cleaning of Equipment. Washington, D.C.: Office of Toxic Substances, U.S. Environmental Protection Agency. Contract 68-02-4248.

2. Transferring to Paper Machine (Release 2)

CEB's standard assumption in cases where the vapor pressure (VP) is less than 0.01 torr is that the release to air due to vaporization of chemicals is negligible. For volatile chemicals (i.e., those with VP $\geq$ 0.01 torr) the *EPA/OAQPS AP-42 Loading Model* will be used. Again, the default parameter values will be based on size of the containers. Drums will be assumed as a reasonable worst-case, if not otherwise specified.

The AP-42 Loading model is used even though the chemical is being unloaded because by unloading one vessel, another is assumed to be loaded at the same time. The AP-42 Loading model is also more conservative than the Penetration model for estimating evaporative releases from open surfaces. Thus, the AP-42 Loading model is the standard default in ChemSTEER for unloading containers.

Note: The amount of chemical released from this source is included in Release 3, discussed below. The AP-42 Loading model is used here to estimate a vapor generation rate to be used by the inhalation exposure model to estimate the worker exposures at this point in the operation (see Exposure A description).

3. Air Release from Papermaking (Release 3)

Paper machines are a source of emissions of volatile organic hazardous air pollutants (HAPs) and volatile organic compounds (VOCs). A field test study of 13 full-scale paper machines located at 11 mills in the U.S. found HAP and VOC emissions at 0.15 lb/t air-dried pulp and 0.44 lb/t air-dried pulp, respectively. Methanol was the major component of the HAP emissions, followed by acetaldehyde, biphenyl, phenol, and chloroform. Factors such as furnish and product type did not significantly affect the HAP emissions from papermaking machines.

Many of the papermaking additives listed in Table 3 do not contain volatile or semi-volatile compounds and as such are not likely to contribute to releases to the air. For nonvolatile chemicals of interest, it is assumed that air releases are negligible. CEB's standard assumption is that the release to air due to vaporization of chemicals is negligible if the pure vapor pressure (VP) is less than 0.01 torr. For chemicals of interest with a vapor pressure greater than or equal to 0.01 torr, it has been estimated that all of the volatile chemicals will be driven off by the heat involved in the papermaking process. The release of the volatile chemical of interest to air from the transfer of the chemical to the papermaking equipment (Release 2, above), as well as from the papermaking equipment during the process (Release 3) can be estimated through the following equation.

$$DRA_{chem} = DMO_{chem} \times (1 - LF_{CR}) \times LF_{AP}$$

Example calculation for daily release to air, using default values and assuming the chemical of interest is volatile:

DRA_{paper} = 6,422 kg/site-day × (1 - 0.03) × 1 = 6,229 kg/site-day

Where:

DRA_{chem}	=	Daily release of chemical of interest to air (kg/site-day)
DMO_{chem}	=	Daily use rate of chemical of interest (kg/site-day)
LF_{CR}	=	Loss fraction of chemical of interest that remains in the shipping container as residue (Defaults: 0.03 for drums, liquid; and 0.01 for solids)
LF_{AP}	=	Loss fraction of volatile chemical of interest released to air from papermaking (Default: 1.0)

Source:

Environment Canada. Collection and Analysis of Chemical Release Data from Canadian Pulp and Paper Mills. Prepared by Crechem Technologies Inc. February 2002.

4. Release from Papermaking to On-site Wastewater Treatment (Release 4)

Most papermaking additive chemicals are released to water. Chemicals that are not incorporated into the final paper product will enter a wastewater stream. While some of the wastewater stream is sent to an on-site treatment system, a portion is recycled into the process for further use. The amount of the wastewater stream that is recycled prior to treatment is measured by the degree of water system closure. The recycling of water at a mill reduces the amount of makeup additives needed. The degree of water system closure will only effect the amount of chemical of interest that is released to wastewater if the closure is 100% (i.e., no wastewater stream). The following equation estimates the amount of the chemical of interest that is released to the on-site wastewater treatment system from the paper machine:

$$DRW_{chem} = DMO_{chem} \times (1 - LF_{CR}) \times (1 - F_{fix})$$

Example calculation for daily release of chemical of interest to on-site wastewater treatment, using default values and assuming the chemical of interest is not volatile:
DRW_{paper} = 6,422 kg/site-day × (1 - 0.03) × (1 - 0) = 6,229 kg/site-day

Where:

DRW_{chem}	=	Daily release of chemical of interest to water from papermaking (kg/site-day)
DMO_{chem}	=	Daily use rate of chemical of interest (kg/site-day)
LF_{CR}	=	Loss fraction of chemical of interest that remains in the shipping container as residue (Defaults: 0.03 for drums, liquid; and 0.01 for solids)
F_{fix}	=	Degree of substance fixation (Default: 0, see Table 5)

In the previous equation, the calculation of (1- F_{fix}) is equivalent to the release of the chemical to wastewater. Using information from the Crechem Technologies Inc. report, releases to wastewater presented below in Table 5 are based on the type of additive the chemical represents. If the type of chemical is not known or is not listed in Table 5, the degree of fixation of a defoamer should be used, since this would result in the most conservative estimate.

Table 5

Chemical Releases to Wastewater Treatment

Type of Additive or Chemical Properties	Degree of Substance Fixation (F_{fix})
Defoamer (default, if no information is known)	0
Retention Aid	0.7-0.9
Wet Strength Resin	0.7-0.9
Alum	0.1-0.3
Sizing (alum + resin)	0.7
Brightener	0.936
Filler	0.95

The previous equation estimates the amount of the chemical of interest that is released to on-site wastewater treatment. Wastewater treatment in the papermaking industry includes primary clarification, chemical flocculation, and secondary biological degradation. This treatment process generates two output streams: the treated liquid effluent and a dewatered sludge. Sludge from primary clarification consists mainly of fibers, fines, and inorganic materials such as fillers. Chemical flocculation generates a considerable amount of sludge depending upon the dosage and type of flocculants used. Biological treatment generates a sludge containing a high organic material content; the quantity generated from aerobic systems can be seven times that from anaerobic systems. The dewatered sludge, which may contain the chemical of interest, will ultimately be released to incineration or landfill. Estimation of on-site biological wastewater treatment efficiency (e.g., how the chemical of interest will partition between the final effluent and sludge) is beyond the scope of a typical CEB engineering assessment; therefore, the amount released to the mill's on-site wastewater treatment system is estimated in this scenario.

Source:

Environment Canada. Collection and Analysis of Chemical Release Data from Canadian Pulp and Paper Mills. Prepared by Crechem Technologies Inc. February 2002.

Occupational Exposure Assessments

Chemical additives are generally handled as either solids, liquids, or slurries in the papermaking process. The form of the additive is a function of the type of additive, the cost of the additive, and handling and storage issues. Most solid additives are pre-mixed with water to form an aqueous solution or slurry of a specific concentration. The additive solution is then pumped and metered into the papermaking operation, or may be added directly at the stock preparation process (e.g., at the beater). Liquid additives are usually stored in bulk and added into the papermaking operation using either gravity feed or metering pumps. Worker exposures to papermaking additives occur at those locations where additives enter the paper stock or are applied on the paper machine. Table 6 presents information on the typical additive forms and the associated exposure risks for each type of papermaking additive listed in Table 3. Note: the nature of papermaking makes the use of some personal protective equipment unsafe.

Table 6

Papermaking Additives and Protection Recommendations

Additive	Typical Form(s)	Protection Recommendations
Acids and Bases	Liquid	Skin and eye protection recommended for strong acids or bases.
Alum	Solid or Liquid (liquid form is more common)	Inhalation protection recommended if nuisance dust occurs. Skin and eye protection recommended for the liquid form.
Sizing Agents Internal	Liquid/Paste/Solid	Skin and eye protection recommended.
Surface	Solid (before make-down)	Inhalation protection recommended if nuisance dust occurs. Not generally a dermal concern.
Dry-strength Adhesives	NA	NA (These chemicals are usually polyacrylamides and are generally nontoxic).
Wet-strength Resins	Liquid	Hazardous classification by OSHA due to the presence of free formaldehyde or epichlorohydrin in the resin. Inhalation of fumes in tanks is an issue and ventilation is required along with skin and eye protection.
Fillers Coloring Materials Optical Brighteners	Solid or Slurry	Inhalation protection recommended if nuisance dust occurs.
Retention Aids Flocculants Drainage Aids	Liquid/Solid (generally nonionic, anionic, or cationic polymers)	Skin and eye protection recommended as these materials are often slippery. Hazards are minimal.
Defoamers	Oil based, water based, or oil/water emulsions	Skin and eye protection is recommended; hazards are minimal.
Pitch Control Chemicals	Liquid (nonionic organic polymers)	Skin and eye protection recommended, but chemicals are generally nonhazardous.
Slimicides	Liquid	Generally pumped and not handled manually. Skin and eye protection is required and ventilation needed where misting is possible.

NA - Not available

Source:

Hipolit, K.J. (Ed.) Chemical Processing Aids in Papermaking: A Practical Guide. Prepared by the Papermaking Additives Committee of the Paper and Board Manufacture Division, Committee Assignment No. 5148. 1992.

Number of Workers per Site

The CBP for 2001 indicates that 160,220 employees were working for paper and paperboard manufacturing facilities associated with NAICS codes 32212 and 32213. Additionally, the most recent data available from the Annual Survey of Manufacturers (ASM) for paper and paperboard mills (NAICS codes 32212 and 32213) indicates that approximately 79% of all employees in 2001 were production workers. It is assumed that production workers are most likely to come in contact with the chemical of interest.

$$NW = \frac{160{,}220 \text{ (workers)} \times 0.79}{555 \text{ (sites)}} = 228 \text{ (workers/site)}$$

Where:

NW	=	Average total number of production workers at a papermaking facility (Default: 228 workers/site)

It should be noted that it is common in the paper and paperboard manufacturing industry to operate three shifts within a 24-hour day. Also, not all of the production workers will be involved in activities within proximity of the stock preparation and paper machine areas.

An alternative approach would be to assume a minimum of three workers per papermaking machine and that a typical facility would have two machines (based on CEB staff engineering experience within paper mills). Since some facilities operate three shifts per day, this would total a minimum of 18 workers per site.

Sources:

U.S. Census. County Business Patterns. U.S. Census Bureau. *http://censtats.census.gov/cgi-bin/cbpnaic/sel.pl* Downloaded September 23, 2003.

U.S. Census. Annual Survey of Manufacturers. U.S. Census bureau. *http://tier2.census.gov/asm/asm.htm*. Downloaded September 23, 2003.

CEB and ERG staff experience within the papermaking industry.

Occupational Exposures

A. <u>Transferring Additive to Paper Machine (Exposure A)</u>

Data on the number of workers involved in transferring additive to paper machines were not found.

<u>Inhalation:</u>

Vapors

If the vapor pressure of the chemical of interest is greater than or equal to 0.001 torr, worker inhalation exposure may occur during the transfer of the chemical of interest. The *EPA/OPPT Mass Balance Model* will be used based on the generation rate from the AP-42 Loading model used in Release 2.

Solids

Workers may be exposed to particulate material (dust) while transferring the nonvolatile chemical of interest to the papermaking equipment. The degree of inhalation exposure to particulate material during transfer operations depends on the weight fraction of the chemical of interest in the transferred material (Y_{add}), the potential concentration of the chemical of interest in the worker's breathing zone (C_s). Since the majority of additives in papermaking are used in large quantities, the OSHA PEL for particulate material (not otherwise regulated) should be used to estimate inhalation exposure. The inhalation exposure to solids from transferring the additive can be calculated through the following equation:

$$I = C_s \times b \times h \times Y_{add}$$

Example calculation for inhalation to solids:
$I = 15 \text{ mg/m}^3 \times 1.25 \text{ m}^3\text{/hr} \times 8 \text{ hr/day} \times 1 = 150 \text{ mg/day}$

Where:

I	=	Inhalation exposure to the chemical of interest (mg/day)
C_s	=	Concentration of the chemical of interest in the worker's breathing zone (default: 15 mg/m^3 OSHA PEL)
b	=	Typical worker breathing rate (Default:1.25 m^3/hr)
h	=	Hours of exposure (Default: 8 hrs/day; if OSHA PEL is used, hours of exposure must be 8 since PEL is TWA)
Y_{add}	=	Weight fraction of chemical of interest in additive component (Default: 1)

Sources:

U.S. EPA, Chemical Engineering Branch. CEB Manual for the Preparation of Engineering Assessments, Volume 1, Contract No. 68-D8-0112. Washington, DC, February 1991.

U.S. EPA, Textile Dye Weighing Monitoring Study. EPA 560/5-90-009. Washington, DC. April 1990.

NIOSH. A Guide to Industrial Respiratory Protection. U.S. Department of Health and Human Services Hew Pub 76-189. 1976.

Dermal:

Workers are expected to have dermal contact with the chemical of interest only during the transfer of the chemical of interest from transport containers to the papermaking machine or during the connection of transfer lines. Using the standard CEB models for screening-level assessments of dermal exposure, the following estimates for worker dermal exposures can be made:

Solids

Use the standard CEB *Direct 2-Hand Contact with Solids* model to calculate the routine handling of solids: resulting in a maximum dermal contact of up to 3,100 mg/day per worker:

$$D_{exp} = 3{,}100 \text{ mg/day} \times Y_{add}$$

Example calculation for dermal exposure to solid chemical of interest:
$D_{exp} = 3{,}100 \text{ mg/day} \times 1 = 3{,}100 \text{ mg/day}$

Where:

D_{exp}	=	Dermal exposure to the chemical of interest (mg/day)
Y_{add}	=	Weight fraction of chemical of interest in additive component (Default: 1)

Liquids

Use the standard CEB *2-Hand Contact with Liquid* model to calculate the routine, incidental handling of liquids (connecting of transfer lines): resulting in a maximum dermal contact of up to 1,800 mg/day per worker:

$$D_{exp} = S \times Qu \times Y_{add}$$

Example calculation for dermal exposure to liquid chemical of interest:
$D_{exp} = 840 \text{ cm}^2 \times 2.1 \text{ mg/day-cm}^2 \times 1 = 1{,}800 \text{ mg/day}$

Where:

D_{exp}	=	Dermal exposure to the chemical of interest (mg/day)
S	=	Surface area of contact (Default: 840 cm^2 for 2 hands)
Qu	=	Quantity of liquid or solid remaining on skin (Default: 2.1 mg/day-cm^2 routine or incidental contact with liquids, 2 hands)
Y_{add}	=	Weight fraction of chemical of interest in additive component (Default: 1)

For acids and bases

For acids or bases with a pH of <2 or a pH of >12 and handled at greater than 50% concentration: Assume negligible dermal exposure, since the handling of acids and bases will require the use of gloves that will mitigate the potential for exposures.

Sources:

CEB Memorandum "Revision to CEB's method for Screening-Level Assessments of Dermal Exposure" from Greg Macek, CEB to CEB staff and contractors; June 2000.

CEB Memorandum "Quality of Engineering Reports" from N. Nguyen, CEB, to CEB staff and contractors; July 1994.

B. Exposure to Additive During Papermaking

The second worker activity with an inhalation exposure potential is from working in or around the papermaking equipment. The paper machine operation is generally very open, and mist exposure is possible, particularly near the wet end operations. Dry end operations typically employ hoods and ventilation controls related to the steam heating of the dryer drums. The degree of enclosure varies, but the heat involved during the dry end operations limits routine exposure to mists and vapors at dry end operations. In addition, dry end operations for the finer paper types (e.g., napkins and tissues) will likely expose workers to nuisance dust. It is assumed that the total number of production workers will have potential exposures to the additive during papermaking.

To estimate inhalation exposure for mists or dusts generated from the paper machine, the following equation can be used:

$$I_m = C_m \times b \times h \times Y_m$$

Example calculation for inhalation to mist:
$I_m = 15\ mg/m^3 \times 1.25\ m^3/hr \times 8\ hr/day \times 1 = 150\ mg/day$

Where:

I_m	=	Inhalation exposure from the mist or dust (mg/day)
C_m	=	Concentration of additive component in the worker's breathing zone (Default:15 mg/m^3 OSHA PEL)
b	=	Typical worker breathing rate (Default:1.25 m^3/hr)
h	=	Hours of exposure (Default: 8 hrs/day; if OSHA PEL is used, hours of exposure must be 8 since PEL is TWA)
Y_m	=	Weight fraction of chemical of interest in mist or dust (Default: 1)

Limitations on the accuracy of mist or dust inhalation estimates arise based on the estimate of airborne concentrations of the mist or dust, the concentration of chemical of interest in the mist or dust, and an assumed breathing rate. Specific data on mist concentration during papermaking activities were not found in the initial information search for this scenario.

Additional sources used but not specifically cited:

- U.S. EPA. Office of Compliance Sector Notebook Project Profile of the Pulp and Paper Industry. EPA/310-R-95-015. Washington DC. September 1995.

- Kirk-Othmer Encyclopedia of Chemical Technology, Volume 18, “Paper”, and “Papermaking Additives”, 1993.

- Springer, A.M. (Ed.) Industrial Environmental Control Pulp and Paper Industry 3rd Edition. 2000.

- U.S. EPA. Pulp and Paper NESHAP: A Plain English Description. EPA/456-R-98-008. Washington DC. November 1998.

- U.S. EPA. Permit Guidance Document Pulp, Paper and Paperboard Manufacturing Point Source Category. EPA 821-B-99-004. Washington DC. June 1999.

Search Process

Other references and web sites reviewed but not used in the preparation of this report include:

TAPPI Web Site Search (including searches on TAPPI Journal articles)
- Papermachine - No relevant hits
- Environmental exposures - No hits
- Papermachine exposures - No hits

Worker exposure - 1 hit
- TAPPI Journal. Identification of Sources of Chemical and Bioaerosol Emissions into the Work Environment During Secondary Treatment of Pulp Mill Effluents. February 2001, Volume 84, No. 2.

Paperloop.com Search
- Papermaking exposures - No hits
- Worker exposure - No hits
- Papermaking machine emissions - No hits
- Wet end emissions - No hits

OSHA Website Search
- Papermaking - No hits
- Worker exposure - (No hits related to papermaking)
- Environmental exposure and papermaking - No hits

Check on TRI Guidance Documents - no TRI Guidance Documents pertain to papermaking operations.

NIOSHtic-2 Database Search

Search on papermaking operations:

Plant Observation Report and Evaluation, Union Camp Corporation, Pulp and Paper Mills, (NIOSH PB88-221304). May 1980: 39 pages.

Preliminary Report of Plants and Processes for Pulp and Paper Mills, Franklin Research Center, Silver Spring, Maryland. (NIOSH PB92-206051). April 1980: 51 pages.