



Polymer Exemption Guidance Manual

POLYMER EXEMPTION GUIDANCE MANUAL

5/22/97

A technical manual to accompany, but not supersede the "Premanufacture Notification Exemptions; Revisions of Exemptions for Polymers; Final Rule" found at 40 CFR Part 723, (60) FR 16316-16336, published Wednesday, March 29, 1995

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1. INTRODUCTION

The Environmental Protection Agency (EPA) published a series of proposed rules (USEPA 1993a-1993d) in the **Federal Register** on February 8, 1993 to announce the Agency's plan to amend premanufacture notification (PMN) regulations for new chemical substances under §5 of the Toxic Substances Control Act (TSCA). Included were proposed amendments to the polymer exemption rule originally published on November 21, 1984 (USEPA 1984) under the auspices of § 5(h)(4) of TSCA and entered into the Code of Federal Regulations (CFR), the administrative rules under which the U.S. Government operates, at 40 CFR Chapter I, Subchapter R, part 723.250.

After the proposed polymer exemption rule was published, the Agency considered public comments, consulted with European counterparts, and utilized the experience gained in the review of over 12,000 polymers in publishing its new final rule for polymer exemptions on March 29, 1995, amending 40 CFR §723.250 (USEPA 1995). The new polymer exemption rule is notably different from that originally published in 1984 and it is the purpose of this technical manual to provide the regulated community with additional insight, so that manufacturers and importers will be able to determine if their new chemical substances are eligible for the polymer exemption under the new rule. Substances submitted before May 30, 1995 are subject to the original rule (USEPA 1984) and its requirements. On or after that date, all polymer exemptions are subject to the new rule and its requirements.

A few notable features of the 1995 Polymer Exemption are as follows:

- Manufacturers and importers are no longer required to submit notice prior to manufacture or import. However, manufacturers and importers must submit an annual report for those exempt polymers whose manufacture or import has commenced for the first time during the preceding calendar year, as stipulated in §723.250(f), and the manufacturer or importer of an exempt polymer must comply with all recordkeeping requirements at §723.250(j).
- A new method can be used for determining which monomers and reactants are considered part of the polymer's chemical identity (modification of the so-called "Two Percent Rule").
- More polymers are now eligible for exemption because previous exclusions have been modified or eliminated. Some of the changes are in regard to halogens, cyano groups, biopolymers and reactive group limitations.
- Certain high molecular weight polymers once considered eligible for submission under the 1984 exemption are not eligible for this exemption.

The EPA hopes this technical manual will: (1) assist the chemical manufacturer or importer in determining whether the PMN substance is a polymer as defined by the polymer exemption rule, (2) guide the manufacturer or importer in determining whether the polymer meets the exemption criteria of the rule and (3) assist the manufacturer or importer in determining whether the polymer is excluded from exemption by certain factors. In addition, this manual provides technical guidance and numerous pertinent examples of decision-making rationales.

The Agency hopes that after reviewing this document prospective manufacturers and importers will be able to decide easily whether the polymer exemption is applicable to any of their new substances. This technical guidance manual is not intended to substitute for or supersede the regulations as found at 40 CFR §723.250 and the **Federal Register** (USEPA 1995). Manufacturers and importers must read those provisions to assure compliance with all the procedural and recordkeeping requirements of the polymer exemption.

2. HISTORY

Section 5 of TSCA contains provisions that allow the Agency to review new chemical substances before they are manufactured or imported. Section 5(a)1 of TSCA requires that persons notify EPA at least 90 days prior to the manufacture or import of a new chemical substance for commercial purposes. A "new" chemical substance is one that is subject to TSCA but is not already included on the TSCA Chemical Substance Inventory. If the Agency determines that a new chemical substance may present an unreasonable risk of injury to human health or the environment or if there is insufficient information to establish that no such risk exists, the Agency may limit the manufacture, processing, distribution in commerce, use, or disposal of the new chemical substance under the authority provided in TSCA §5(e).

From the beginning of the PMN program in 1979 until 1984 all new chemical substances, including polymers, were subject to the full reporting requirements of the premanufacture notification process. Under §5(h)(4) the Agency has authority to promulgate rules granting exemptions from some or all of the premanufacture requirements for new chemicals if the Agency determines that the manufacturing, processing, distribution in commerce, use, or disposal of a new chemical substance will not present an unreasonable risk of injury to human health or the environment.

Through its experience in reviewing new chemical substances, the Agency identified certain criteria to determine which polymers were most unlikely to present an unreasonable risk of injury to human health or the environment. This experience led to the original polymer exemption rule under §5(h)(4) allowing polymers that met certain criteria under these conservative guidelines to be exempt from some of the reporting requirements for new chemicals (USEPA 1984).

Since the EPA published the 1984 TSCA polymer exemption rule, the Agency has reviewed over 10,000 polymer submissions under the standard 90 day PMN review process and an additional 2,000 polymer exemption notices. With the experience gained by the review of this large number of submissions, the Agency reevaluated the criteria used to identify those polymers which were unlikely to present unreasonable risks. This led to the proposal of a revised polymer exemption rule that would increase the number of polymers qualifying for exemption and enable the Agency to concentrate its limited resources on those polymers that do not meet the polymer exemption criteria and on non-polymeric new chemical substances that may present greater risks. The amendments are expected to result in resource savings for industry as well as the EPA.

The new polymer exemption rule amends appropriate sections of 40 CFR 723.250 to allow certain polymers to be exempt from the reporting requirements for new chemicals and imposes new restrictions on a limited set of polymers that were previously eligible for the exemption (USEPA 1993d). To be eligible for the exemption, a new chemical substance must: 1) meet the polymer definition, 2) meet one of three exemption criteria and 3) not be excluded. The definition of polymer, for purposes of the new exemption, is found at 40 CFR §723.250(b). There are now three exemption types, located at 40 CFR §723.250(e)(1), (e)(2), and (e)(3), subsequently referred to as the (e)(1), (e)(2), and (e)(3) criteria. Excluded categories are listed at 40 CFR §723.250(d) of the new rule.

The definition of polymer, the key components of each of the three exemption types, and the categories excluded from the exemption are discussed below. The remainder of this technical manual provides prospective submitters with information helpful for establishing whether or not their new chemical substances meet the exemption criteria.

The **(e)(1) exemption** concerns polymers with a number-average molecular weight (NAVG MW) in a range that is greater than or equal to 1,000 (≥ 1000) daltons and less than 10,000 ($<10,000$) daltons.

Dalton - precisely 1.0000 atomic mass unit or 1/12 the mass of a carbon atom of mass 12. Hence, a polymer with a molecular weight of 10,000 atomic mass units has a mass of 10,000 daltons.

For the **(e)(1) exemption**, oligomer content must be less than 10 percent by weight below 500 daltons and less than 25% by weight below 1,000 daltons. The polymer must also meet functional group criteria to be described in a later section of this manual.

Oligomer (in the context of the rule and this manual) - a low molecular weight species derived from the polymerization reaction. The Organization for Economic Cooperation and Development (OECD) has a draft guidelines document¹ for determining the low molecular weight polymer content.

For the **(e)(2) exemption**, the NAVG MW for eligible polymers must be greater than or equal to 10,000 daltons and these polymers must have oligomer content less than two percent below 500 daltons and less than 5 percent below 1,000 daltons.

The **(e)(3) exemption** concerns certain polyester polymers (as defined at §723.250(b)) composed solely of monomers and reactants from the list as found at §723.250**(e)(3)**.

In addition to meeting the specific criteria of one of the three exemption types described above, the new polymer must not fall into any of the prohibited categories listed at §723.250(d) of the new rule. This section of the amended rule specifically excludes certain polymers from the reduced reporting requirements of the polymer exemption: certain cationic polymers; polymers that do not meet elemental restrictions; polymers that degrade, decompose, or depolymerize; and polymers that are produced from monomers and/or other reactants that are not on the TSCA inventory or otherwise exempted from full PMN reporting under a §5 exemption. Some highly water-absorbing, high molecular weight polymers are also specifically prohibited. Any new chemical polymer substance that does not meet the polymer definition, does not meet any of the **(e)(1)**, **(e)(2)**, or **(e)(3)** exemptions, or is specifically excluded from the polymer exemption is subject to the full PMN reporting requirements.

3. DEFINITIONS

For a new polymer to be eligible for the exemption it must meet distinct criteria set forth in the 1995 polymer exemption rule. Much of the terminology used in these criteria is explained in this and subsequent sections of the guidance manual. Note that the definitions provided herein are those used in the new polymer exemption rule, and that these terms may not necessarily have the same meaning as commonly used in an academic or industrial setting. Careful attention must be paid to the definitions contained in the new polymer exemption rule when determining eligibility.

The polymer definition has been revised to conform with the international definition recently adopted by the OECD as a result of the *Experts on Polymers Meetings* held in Toronto, Canada (January 1990), Paris, France (October 1991), and Tokyo, Japan (April 1993), in which the Agency participated. The definition was agreed upon in May 1993 by the OECD member countries, including the United States, Canada, Japan, and member nations of the European Union. The definitions of polymer and other important terms as used in the new polymer exemption rule are:

Polymer - a chemical substance consisting of molecules characterized by the sequence of one or more types of monomer units and comprising a simple weight majority of molecules containing at least 3 monomer units which are covalently bound to at least one other monomer unit or other reactant and which consists of less than a simple weight majority of molecules of the same molecular weight. Such molecules must be distributed over a range of molecular weights wherein differences in the molecular weight are primarily attributable to differences in the number of monomer units.

Monomer - a chemical substance that is capable of forming covalent bonds with two or more like or unlike molecules under the conditions of the relevant polymer-forming reaction used for the particular process.

Monomer unit - the reacted form of the monomer in a polymer.

Sequence - a continuous string of monomer units within the molecule that are covalently bonded to one another and are uninterrupted by units other than monomer units.

Reactant - a chemical substance that is used intentionally in the manufacture of a polymer to become chemically a part of the polymer composition. (Reactants include monomers, chain transfer and crosslinking agents, monofunctional groups that act as modifiers, other end groups or pendant groups incorporated into the polymer. For example, sodium hydroxide is considered a reactant when the sodium ion becomes part of the polymer molecule as a counter ion.)

Other reactant - a molecule linked to one or more sequences of monomer units but which under the relevant reaction conditions used for the particular process cannot become a repeating unit in the polymer structure. (This term is used primarily in applying the concept of sequence in the definition of a polymer).

Polymer molecule - a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant.

Internal monomer unit - a monomer unit of a polymer molecule that is covalently bonded to at least two other molecules. Internal monomer units of polymer molecules are chemically derived from monomer molecules that have formed covalent bonds between two or more other monomer molecules or other reactants.

Number-Average Molecular Weight - the arithmetic average (mean) of the molecular weights of all molecules in a polymer. (This value should not take into account unreacted monomers and other reactants, but must include oligomers.)

4. ELIGIBILITY REQUIREMENTS

In order for a new chemical substance to be eligible for exemption under the amended rule, it must meet the following requirements:

- The substance must meet the definition of a polymer as defined in §723.250(b);
- The substance must not be specifically excluded from the polymer exemption by §723.250(d); and
- The substance must meet one of the (e)(1), (e)(2), or (e)(3) criteria.

4.1 MEETING THE DEFINITION OF A POLYMER AT 40 CFR §723.250(b)

For deciding if a substance meets the definition of a polymer these sequence and distribution criteria must be met:

- > 50 percent of molecules must be composed of a sequence of at least 3 monomer units plus at least one additional monomer unit or

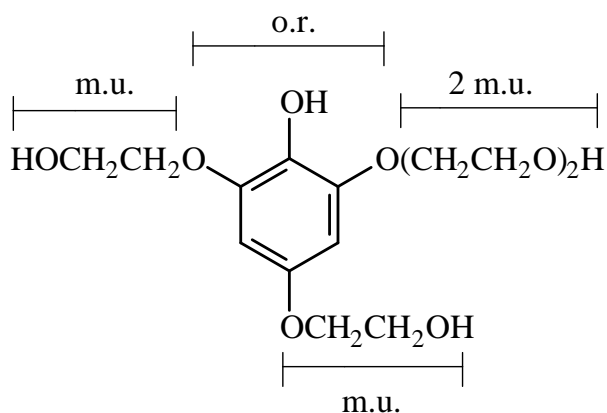
other reactant. (In other words, > 50 percent of the substance must be polymer molecules.)

- The amount of polymer molecules of any one molecular weight cannot exceed 50 weight percent.

The following examples illustrate the analysis of substances with regard to the polymer definition criteria mentioned above. Some of these have been taken from the Chairman's Report² of the Chemicals Group and Management Committee at the Third Meeting of OECD Experts on Polymers (Tokyo, April 14-16 1993) in which the Agency participated. In the figures, 'o.r.' refers to 'other reactant,' and 'm.u.' refers to 'monomer unit.' Examples 1-5 illustrate the sequence criteria for defining a polymer molecule. In Examples 1-3 the relevant polymer-forming reaction is ethoxylation with ethylene oxide.

Example 1:

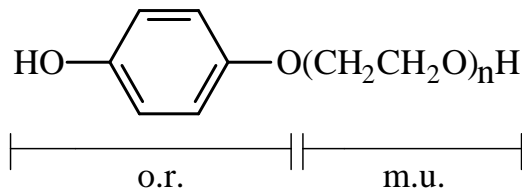
Figure 1
Ethoxylated Benzenetetrol:



Example 1 does not meet the sequence criterion and is therefore not a polymer molecule. Under the reaction conditions, the phenol hydroxy group can neither react with another phenol hydroxy nor an opened epoxide. Therefore, phenolic precursor is an 'other reactant,' (o.r.). In the molecule shown, there is no sequence of three monomer units (m.u.) from ethylene oxide.

Example 2:

Figure 2
Ethoxylated Hydroquinone:



The Example 2 molecule, produced from the ethoxylation of hydroquinone, would meet the sequence criterion if $n \geq 3$ and therefore would be a polymer molecule. Hydroquinone would be an 'other reactant' because the phenol hydroxyl can react with neither another phenol hydroxyl nor an opened epoxide, under the reaction conditions.

Example 5 meets the sequence criterion and therefore would be a polymer molecule. It has an unbroken chain of three monomer units and one other reactant.

Examples 6, 7, and 8:

Examples 6-8 illustrate the sequence and distribution criterion of the new polymer exemption rule.

**Table 1
Distribution Criteria Examples 6, 7, and 8: Ethoxylated Alcohols**

SPECIES	o.r. + m.u.	EXAMPLE 6	EXAMPLE 7	EXAMPLE 8
RO.EO.H	1 + 1	5%	25%	8%
RO.EO.EO.H	1 + 2	20%	35%	20%
RO.EO.EO.EO.H	1 + 3	30%	20%	52%
RO.EO.EO.EO.EO.H	1 + 4	40%	10%	10%
RO.EO.EO.EO.EO.EO.H	1 + 5	5%	10%	10%

For these examples, 'EO' is a monomer unit derived from ethylene oxide, and 'RO' is an other reactant derived from an alcohol. Example 6 meets the definition of a polymer because >50 percent of the substance has molecules of at least 3 monomer units in sequence and <50 percent of each species (same molecular weight components) is present. Example 7 does not meet the definition of polymer because <50 percent of substance has molecules of at least 3 monomer units plus at least one additional monomer unit or other reactant. Example 8 does not meet the definition of polymer because >50 percent of one molecular weight species is present.

Example 9:

Consider the enzyme pepsin and the sequence and distribution criteria of the new polymer exemption rule's definition of a polymer substance. Although pepsin meets the sequence requirements of the polymer definition, the molecules will always have the same distinct molecular weight, corresponding to the sum of the molecular weights of the amino acid monomer units which comprise the specific protein sequence of the enzyme. As such it has a majority of molecules having identical weight and will not meet that portion of the new rule's definition of a polymer.

On the other hand, a lipoprotein or mucoprotein with its attachments intact might satisfy the sequence and distribution criteria. The lipo- or muco- portions can be quite variable in quantity and this could cause enough variation in weight of the polymer molecules.

4.2. SUBSTANCES EXCLUDED FROM THE EXEMPTION AT 40 CFR §723.250(d)

Certain categories of polymers are ineligible for exemption under the new polymer exemption rule because the Agency cannot determine whether these substances can be reasonably anticipated to present an unreasonable risk of injury to human health or the environment. For a discussion of the history behind the selection of these categories consult the preamble to the 1995 polymer exemption rule (USEPA 1995). The following sections discuss the excluded categories.

4.2.1. EXCLUSIONS FOR CATIONIC AND POTENTIALLY CATIONIC POLYMERS

Cationic polymers and those polymers which are reasonably anticipated to become cationic in the natural aquatic environment are excluded from the exemption and may not be manufactured under it. The principal concern is the toxicity toward aquatic organisms.

Cationic polymer - a polymer that contains a net positively charged atom(s) or associated group(s) of atoms covalently linked to the polymer molecule. This includes, but is not limited to phosphonium, sulfonium, and ammonium cations.

Potentially cationic polymer - a polymer containing groups that are reasonably anticipated to become cationic. This includes, but is not limited to, all amines (primary, secondary, tertiary, aromatic, etc.) and all isocyanates (which hydrolyze to form carbamic acids, then decarboxylate to form amines).

Reasonably anticipated means that a knowledgeable person would expect a given physical or chemical composition or characteristic to occur, based on such factors as the nature of the precursors used to manufacture the polymer, the type of reaction, the type of manufacturing process, the products produced in the polymerization, the intended uses of the substance, or associated use conditions.

4.2.1.1. CATIONIC POLYMERS NOT EXCLUDED FROM EXEMPTION

Through its experience reviewing thousands of polymers, the Agency has determined that two categories of cationic and potentially cationic polymers would not pose an unreasonable risk of injury to human health or the environment. These two types are **not** excluded from consideration for the exemption and are as follows:

- Cationic or potentially cationic polymers that are solids, are neither water soluble nor dispersible in water, are only to be used in the solid phase, and are not excluded from exemption by other factors, and
- Cationic or potentially cationic polymers with low cationic density (the percent of cationic or potentially cationic species with respect to the overall weight of polymer) which would not be excluded from the exemption by other factors.

For a polymer to be considered to have low cationic density, the concentration of cationic functional groups is limited to a functional group equivalent weight of greater than or equal to 5,000 daltons.

Functional group equivalent weight (FGEW) - the weight of polymer that contains one equivalent of the functional group; or the ratio of number-average molecular weight (NAVG MW) to the number of functional groups in the polymer. The methods for calculating the FGEW are described in a later section.

Example 10:

As an example of the cationic density requirement, consider the reaction of precisely equal molar amounts of ethanediamine and phthalic acid, resulting in a polyamide (polymer) with an equal number of unreacted amine and unreacted carboxylic acid groups. This would be equivalent to a sample of polymer molecules that would have (on average) one end group that was an unreacted amine (potentially cationic) and the other end group an unreacted carboxylic acid. For this polymer to be eligible for the exemption it must have a minimum NAVG MW of 5,000 daltons which would give the amine FGEW as 5,000 daltons (1 amine termination per 5,000 MW of polymer).

4.2.2. EXCLUSIONS FOR ELEMENTAL CRITERIA

A polymer manufactured under the 1995 rule must contain as an integral part of its composition at least two of the atomic elements of carbon, hydrogen, nitrogen, oxygen, sulfur, or silicon (**C, H, N, O, S, Si**).

In addition to the six elements listed above, only certain other elements are permitted either as counterions or as an integral part of the polymer. These additional elements are as follows: fluorine, chlorine, bromine and iodine (**F, Cl, Br** and **I**) when covalently bonded to carbon, and the monatomic counterions chloride, bromide, and iodide (**Cl-**, **Br-** and **I-**). The fluoride anion, (**F-**) is not permitted. This decision was based on data obtained by the Agency. Other permitted monatomic cations are sodium, magnesium, aluminum, potassium, and calcium (**Na+**, **Mg+2**, **Al+3**, **K+** and **Ca+2**). Allowed at less than 0.20 weight percent total (in any combination) are the atomic elements lithium, boron, phosphorus, titanium, manganese, iron, nickel, copper, zinc, tin and zirconium (**Li, B, P, Ti, Mn, Fe, Ni, Cu, Zn, Sn, and Zr**). No other elements are permitted, except as impurities.

4.2.3. EXCLUSIONS FOR DEGRADABLE OR UNSTABLE POLYMERS

A polymer is not eligible to be manufactured under the new exemption rule if the polymer is designed or reasonably anticipated to substantially degrade, decompose, or depolymerize, including those polymers that could substantially decompose after manufacture and use, even though they are not actually intended to do so. For purposes of this section the following definition applies:

Degradation, decomposition, or depolymerization - a type of chemical change in which a polymeric substance breaks down into simpler, smaller weight substances as the result of (for example) oxidation, hydrolysis, heat, sunlight, attack by solvents or microbial action.

4.2.4. EXCLUSIONS BY REACTANTS

A polymer may contain at more than two percent by weight only those reactants and monomers that are either: on the TSCA Chemical Substance Inventory, granted a \$5 exemption, (a low-volume exemption; a polymer exemption under the 1984 rule; etc.), excluded from reporting or a non-isolated intermediate. Monomers and reactants that do not fit one of these categories would render a polymer ineligible for the polymer exemption. This applies to both manufactured and imported polymers. (See section 5.2. of this manual for a discussion of the so-called "Two Percent Rule").

Monomers and reactants incorporated or charged at greater than two percent in a polymer are considered part of the chemical identity of the new polymer. (See Section 5.2. on the "Two Percent Rule.") Monomers and reactants which are not on the Inventory and do not have a \$5 exemption may be used at less than or equal to two percent provided that those monomers and reactants will not introduce into the polymer any elements, properties, or functional groups that would render the polymer ineligible for the exemption. However, in practice, the use of non-Inventory monomers or reactants at two percent or less applies only to imported polymers since domestic manufacturers may not distribute or use any substance unless it is on the TSCA Inventory or exempt from TSCA reporting requirements. In other words, non-Inventory monomers and reactants may be handled domestically only if they are intermediates made *in situ* and are not isolated, or if they are already exempt.

4.2.5. EXCLUSIONS FOR WATER-ABSORBING POLYMERS

Water-absorbing polymers with number-average molecular weight (NAVG MW) of 10,000 daltons and greater are excluded from exemption. A history describing how the EPA came to select this NAVG MW and the level of water absorptivity to be excluded is given in the preamble to the new rule. The Agency's definition of water-absorbing is given below:

Water-absorbing polymer means a polymeric substance that is capable of absorbing its weight of water.

4.3. CATEGORIES WHICH ARE NO LONGER EXCLUDED FROM EXEMPTION

Three exclusions have been dropped from the new polymer exemption rule because the Agency now believes that other provisions of the new rule will exclude any polymers that would pose an unreasonable risk of injury to human health or the environment. The three types of polymers that are no longer automatically excluded from the exemption are: (1) polymers containing less than 32 percent carbon; (2) polymers manufactured from reactants containing halogen atoms (see section 4.2.2 of this manual) or cyano groups; and (3) biopolymers. To be manufactured under the exemption these polymers must meet all of the criteria of the new rule. For example, in the biopolymer category, most enzymes and polypeptides will not meet the polymer definition because of the requirement that the molecular weight of the polymer must be distributed over a range (no one molecular weight species can be present in a simple majority). Some DNA, RNA or polysaccharide substances may meet the molecular weight distribution criterion but fail because of reactivity (reactive group content, degradability, etc.), cationic potential, or water-absorbing properties.

4.4. MEETING EXEMPTION CRITERIA at 40 CFR §723.250(e)

Providing the new polymer meets the definition of a polymer at §723.250(b) and the polymer is not automatically excluded by section §723.250(d), the polymer must also meet one or more of the criteria listed in §723.250 (e)(1), (e)(2), or (e)(3) to be manufactured or imported under a polymer exemption.

4.4.1. THE (e)(1) EXEMPTION CRITERIA

In order to be manufactured or imported under §723.250(e)(1), the polymer must have a NAVG MW equal to or greater than 1,000 daltons and less than 10,000 daltons. (See section 5.1., for determining NAVG MW.) The polymer also must contain less than 10 percent oligomer content of molecular weight below 500 daltons and less than 25 percent oligomer content of molecular weight below 1,000 daltons. In addition, (e)(1) polymers have reactivity constraints. The polymer must have either: no reactive functional groups; only low-concern functional groups; or it must have a functional group equivalent weight (FGEW) above threshold levels for moderate- and high-concern functional groups in order to remain eligible for the exemption. (See section 5.3., "Calculating Functional Group Equivalent Weight," in this manual.)

Reactive functional group - an atom or associated group of atoms in a chemical substance that is intended or can be reasonably anticipated to undergo facile chemical reaction.

The following sections describe the reactive functional groups in the low-concern, moderate-concern and high-concern categories.

4.4.1.1. LOW-CONCERN FUNCTIONAL GROUPS AND THE (e)(1) EXEMPTION

Low-concern functional groups defined in §723.250(e)(1)(ii)(A) may be used without limit. These groups are so categorized because they generally lack reactivity in biological settings. The low-concern reactive functional groups are: carboxylic acid groups; aliphatic hydroxyl groups; unconjugated olefinic groups that are considered "ordinary;" butenedioic acid groups; those conjugated olefinic groups contained in naturally-occurring fats, oils, and carboxylic acids; blocked isocyanates (including ketoxime-blocked isocyanates); thiols; unconjugated nitrile groups; and halogens (not including reactive halogen-containing groups such as benzylic or allylic halides).

Ordinary olefinic groups - unconjugated olefinic groups that are **not** specifically activated either by being part of a larger functional group, such as a vinyl ether, or by other activating influences, such as the strongly electron-withdrawing sulfone functionality (in a vinyl sulfone system).

In addition, carboxylic esters, ethers, amides, urethanes and sulfones are implicitly permitted because polyesters, polyethers, polyamides, polyurethanes, and polysulfones are among the types of polymers allowed under the exemption, as long as these functional groups have not been modified to enhance their reactivity. One such group that would **not** be allowed is the dinitrophenyl ester of a carboxylic acid, which is far more reactive due to the activating functionality.

In summary, if a substance (1) meets the definition of a polymer, (2) is not excluded by §723.250(d), (3) has a NAVG MW greater than or equal to 1000 daltons and less than 10,000 daltons, (4) contains only the low-concern reactive functional groups, and (5) meets oligomer content criteria (<10 percent below 500 daltons and <25 percent below 1000 daltons), the new substance may be manufactured under a polymer exemption.

4.4.1.2. MODERATE-CONCERN FUNCTIONAL GROUPS AND THE (e)(1) EXEMPTION

Moderate-concern groups defined in §723.250(e)(1)(ii)(B) may be used with functional group equivalent weight (FGEW) constraints. Each functional group present from category (B) must have a FGEW of greater than or equal to 1,000 daltons. For a polymer containing no type (C) groups (see section 4.4.1.3 for when type (C) groups are present), the FGEW_{combined} must be greater than or equal to 1,000 daltons. (The method for calculating a FGEW_{combined} is covered in section 5.3. of this manual). The moderate-concern reactive functional groups are: acid halides; acid anhydrides; aldehydes; hemiacetals; methylolamides; methylolamines; methylolureas; alkoxy silanes bearing alkoxy groups greater than C₂; allyl ethers; conjugated olefins (except those in naturally-occurring fats, oils, and carboxylic acids); cyanates; epoxides; imines (ketimines and aldimines); and unsubstituted positions ortho- and para- to a phenolic hydroxyl group.

In summary, if a substance (1) meets the definition of a polymer, (2) is not excluded by any of the provisions of §723.250(d), (3) has a NAVG MW greater than or equal to 1000 daltons and less than 10,000 daltons, (4) has individual FGEWs and a FGEW_{combined} greater than or equal to 1,000 daltons for moderate-concern groups (when high-concern groups are not present, but low-concern groups may be present without limit), and (5) meets oligomer content criteria (<10 percent below 500 daltons and <25 percent below 1000 daltons), the new substance may be manufactured under a polymer exemption.

4.4.1.3. HIGH-CONCERN FUNCTIONAL GROUPS AND THE (e)(1) EXEMPTION

Reactive groups not defined by (e)(1)(ii)(A) or (B) fall into category (e)(1)(ii)(C), the high-concern reactive functional groups. These may be used with more restriction than moderate-concern groups alone. If a polymer contains type (C) reactive functional groups, each type (C) functional group present must meet a 5,000 dalton minimum permissible limit, each type (B) group present must meet the 1,000 dalton limit and the polymer must have a

FGEW_{combined} of greater than or equal to 5,000 daltons. A FGEW_{combined} calculation takes into account all type (C) and type (B) reactive groups. (This type of calculation is covered in section 5.3. of this manual.) Therefore, if a substance containing category (e)(1)(ii)(C) functional groups meets the definition of a polymer, is not excluded by any of the provisions of §723.250(d), has a NAVG MW greater than or equal to 1,000 daltons and less than 10,000 daltons, has a FGEW_{combined} greater than 5,000 daltons, meets the individual type (B) and (C) FGEW limits of 1,000 and 5,000, respectively, and the polymer meets oligomer content criteria (<10 percent below 500 daltons and <25 percent below 1000 daltons) the new substance may be manufactured under a polymer exemption.

Table 2 summarizes the FGEW_{combined} minimum permissible levels as discussed in the preceding (e)(1) exemption criteria section of this manual. In the table, the 'X' marks which type of group (or groups) is present from the categories: low-concern, moderate-concern, and high-concern.

Table 2
FGEW_{combined} Summary

Low- Concern	X			X	X		X
Moderate- Concern		X		X		X	X
High- Concern			X		X	X	X
Minimum FGEW _{combined}	None*	1,000	5,000	1,000**	5,000**	5,000	5,000**

* There are no FGEW limits for polymers containing only low-concern (type A, also known as (e)(1)(ii)(A)) functional groups.

** When calculating FGEW_{combined} for substances with moderate (Type (B)) and/or high-concern (Type (C)) functional groups, low-concern groups (Type (A)) are not included in the calculation.

4.4.2. THE (e)(2) EXEMPTION CRITERIA

Those polymers having NAVG Mws exceeding the limits of §723.250(e)(1) are subject to §723.250(e)(2). Hence, this section covers polymers with NAVG Mws greater than or equal to 10,000 daltons. The oligomeric content of these higher molecular weight polymers must be less than two percent for species with molecular weight less than 500 daltons, and must be less than 5 percent for species of molecular weight less than 1,000 daltons. There are no functional group restrictions for the (e)(2) exemption, but the substance must not be excluded from exemption by any of the provisions found at §723.250(d). For example, water-absorbing polymers and cationic or potentially cationic polymers in this weight range are excluded from exemption by §723.250(d).

Therefore, if a substance meets the definition of a polymer, is not excluded by any of the provisions of §723.250(d), has a NAVG MW greater than or equal to 10,000, and meets the oligomer content criteria (less than two percent below 500 daltons and <5 percent below 1,000 daltons), the new substance may be manufactured under a polymer exemption.

4.4.3. THE (e)(3) EXEMPTION CRITERIA

Section 723.250(e)(3) provides for the exemption of manufactured or imported polyesters which have been prepared exclusively from a list of feedstocks identified in section (e)(3) of the new rule. To qualify for this exemption, each monomer or reactant in the chemical identity of the polymer (charged at any level) must be on the list. At this writing (5/22/97), six entries on the list are not on the TSCA Inventory. Therefore, these six monomers and reactants are not allowed for use in domestic manufacture.

Just as for all other exempted polymers, polyesters that are allowed an exemption under (e)(3) must meet the definition of a polymer and must not be excluded from exemption by §723.250(d). For example, excluded from an (e)(3) exemption are biodegradable polyesters and highly water-absorbing polyesters with number-average molecular weights (NAVG MW) greater than 10,000 daltons.

The following is the list from which all monomers and reactants in (e)(3)-exempted polymers must be taken. They are listed by Chemical Abstracts Index Names and Registry Numbers (where available). A "√" identifies the six substances not on the TSCA Inventory, as of this writing.

Table 3
The (e)(3) Monomer and Reactant List
(in order by CAS Registry Number)

[56-81-5]	1,2,3-Propanetriol
[57-55-6]	1,2-Propanediol
[65-85-0]	Benzoic acid
[71-36-3]**	1-Butanol
[77-85-0]	1,3-Propanediol, 2-(hydroxymethyl)-2-methyl-
[77-99-6]	1,3-Propanediol, 2-ethyl-2-(hydroxymethyl)-
[80-04-6]	Cyclohexanol, 4,4'-(1-methylethylidene)bis-
[88-99-3]	1,2-Benzenedicarboxylic acid
[100-21-0]	1,4-Benzenedicarboxylic acid
[105-08-8]	1,4-Cyclohexanedimethanol
[106-65-0]	Butanedioic acid, dimethyl ester
[106-79-6]	Decanedioic acid, dimethyl ester
[107-21-1]	1,2-Ethandiol
[107-88-0]	1,3-Butanediol
[108-93-0]	Cyclohexanol
[110-15-6]	Butanedioic acid
[110-17-8]	2-Butenedioic acid (E)-
[110-40-7]	Decanedioic acid, diethyl ester
[110-63-4]	1,4-Butanediol
[110-94-1]	Pentanedioic acid,
[110-99-6]	Acetic acid, 2,2'-oxybis-
[111-14-8]	Heptanoic acid
[111-16-0]	Heptanedioic acid
[111-20-6]	Decanedioic acid
[111-27-3]	1-Hexanol
[111-46-6]	Ethanol, 2,2'-oxybis-
[112-05-0]	Nonanoic acid
[112-34-5]	Ethanol, 2-(2-butoxyethoxy)-
[115-77-5]	1,3-Propanediol, 2,2-bis(hydroxymethyl)-
[120-61-6]	1,4-Benzenedicarboxylic acid, dimethyl ester
[121-91-5]	1,3-Benzenedicarboxylic acid
[123-25-1]	Butanedioic acid, diethyl ester
[123-99-9]	Nonanedioic acid
[124-04-9]	Hexanedioic acid
[126-30-7]	1,3-Propanediol, 2,2-dimethyl-
[141-28-6]	Hexanedioic acid, diethyl ester
[142-62-1]	Hexanoic acid
[143-07-7]	Dodecanoic acid
[144-19-4]	1,3-Pentanediol, 2,2,4-trimethyl-
[505-48-6]	Octanedioic acid
[528-44-9]	1,2,4-Benzenetricarboxylic acid
[624-17-9]	Nonanedioic acid, diethyl ester
[627-93-0]	Hexanedioic acid, dimethyl ester
[629-11-8]	1,6-Hexanediol
[636-09-9]	1,4-Benzenedicarboxylic acid, diethyl ester
[693-23-2]	Dodecanedioic acid
[818-38-2]	Pentanedioic acid, diethyl ester
[1119-40-0]	Pentanedioic acid, dimethyl ester
[1459-93-4]	1,3-Benzenedicarboxylic acid, dimethyl ester

[1732-08-7] Heptanedioic acid, dimethyl ester
 [1732-09-8] Octanedioic acid, dimethyl ester
 [1732-10-1] Nonanedioic acid, dimethyl ester
 [1852-04-6] Undecanedioic acid
 [2163-42-0] 1,3-Propanediol, 2-methyl
 [3302-10-1] Hexanoic acid, 3,3,5-trimethyl-
 [8001-20-5]* Tung oil
 [8001-21-6]* Sunflower oil
 [8001-22-7]* Soybean oil
 [8001-23-8]* Safflower oil
 [8001-26-1]* Linseed oil
 [8001-29-4]* Cottonseed oil
 [8001-30-7]* Corn oil
 [8001-31-8]* Coconut oil
 [8002-50-4]* Fats and glyceridic oils, menhaden
 [8016-35-1]* Fats and glyceridic oils, oiticica
 [8023-79-8]* Palm kernel oil
 [8024-09-7]* Oils, walnut
 [13393-93-6] 1-Phenanthrenemethanol, tetradecahydro-1,4a-dimethyl-7-(1-methylethyl)-
 [25036-25-3] Phenol, 4,4'-(1-methylethylidene)bis-, polymer with 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxymethylene)]-bis[oxirane]
 [25119-62-4] 2-Propen-1-ol, polymer with ethenylbenzene
 [25618-55-7] 1,2,3-Propanetriol, homopolymer
 [61788-47-4]* Fatty acids, coco
 [61788-66-7]* Fatty acids, vegetable-oil
 [61788-89-4]* Fatty acids, C18-unsatd., dimers
 [61789-44-4]* Fatty acids, castor oil
 [61789-45-5]* Fatty acids, dehydrated castor oil
 [61790-12-3]* Fatty acids, tall-oil
 [67701-08-0]* Fatty acids, C16-18 and C18-unsatd.
 [67701-30-8]* Glycerides, C16-18 and C18-unsatd.
 [68037-90-1]* Silsesquioxanes, Ph Pr
 [68132-21-8]* Oils, perilla
 [68153-06-0]* Fats and glyceridic oils, herring
 [68308-53-2]* Fatty acids, soya
 [68424-45-3]* Fatty acids, linseed oil
 [68440-65-3]* Siloxanes and silicones, di-Me, di-Ph, polymers with Ph silsesquioxanes, methoxy-terminated
 [68957-04-0]* Siloxanes and silicones, di-Me, methoxy Ph, polymers with Ph silsesquioxanes, methoxy-terminated
 [68957-06-2]* Siloxanes and silicones, Me Ph, methoxy Ph, polymers with Ph silsesquioxanes, methoxy- and Ph-terminated
 [72318-84-4]* Methanol, hydrolysis products with trichlorohexylsilane and trichlorophenylsilane
 [84625-38-7]* Fatty acids, sunflower-oil
 [68649-95-6]* Linseed oil, oxidized
 [68953-27-5]* Fatty acids, sunflower-oil, conjugated
 [91078-92-1]* √ Fats and glyceridic oils, babassu
 [93165-34-5]* √ Fatty acids, safflower-oil
 [93334-41-9]* √ Fats and glyceridic oils, sardine
 [120962-03-0]* Canola oil
 [128952-11-4]* √ Fats and glyceridic oils, anchovy
 [No Registry #]* √ Fatty acids, tall-oil, conjugated
 [No Registry #]* √ Oils, cannabis

* Designates chemical substances of unknown or variable composition, complex reaction products, or biological materials (UVCB substances). The CAS Registry Numbers for UVCB substances are not used in Chemical Abstracts and its indexes.

** 1-Butanol may not be used in a substance manufactured from fumaric or maleic acid because of potential risks associated with esters which may be formed by reaction of these reactants.

5. NUMERICAL CONSIDERATIONS

There are several numerical criteria to consider when deciding if a polymer is eligible for an exemption:

1). **Number-average molecular weight** (NAVG MW) is one of the criteria defining whether an eligible polymer fits an (e)(1) or (e)(2) exemption; in the case of a water-absorbing polymer, NAVG MW defines whether or not the polymer will be excluded from exemption due to the 10,000 dalton restriction. Section 5.1., expounds on NAVG MW determination.

2). The **"Two Percent Rule"** governs whether a monomer or other reactant is part of the chemical identity. Substances that are considered by the Agency as automatically part of the chemical identity of the polymer (those monomers or reactants used at greater than two percent composition) must be on the TSCA Inventory, excluding from reporting or otherwise exempt under section 5 of TSCA. For **(e)(1)** and **(e)(2)** exemptions, imported polymers may have monomers or reactants at less than or equal to 2 percent which are not on the Inventory; whereas in the case of domestic manufacture under an **(e)(1)** or **(e)(2)** exemption, all monomers and reactants must either be: on the Inventory; a non-isolated intermediate; otherwise exempt; or excluded from reporting. For **(e)(3)** polymers, all monomers and reactants, regardless of charge must be from the **(e)(3)** list, but only those charged at greater than 2 percent will be part of the identity. Section 5.2. explains the so-called "Two Percent Rule" and its determination.

3). The **functional group equivalent weight** (FGEW) is a measure of the concentration of functional groups of moderate- and high-concern in the polymer. This is an important factor in determining eligibility for polymers with NAVG MW greater than or equal to 1,000 daltons and less than 10,000 daltons. It is also important in determining whether a cationic polymer is excluded. Section 5.3., below, explains the determination of FGEW.

5.1. CALCULATING NUMBER-AVERAGE MOLECULAR WEIGHT

The rationale and theoretical basis for determining number-average molecular weight (NAVG MW) and brief summaries of the preferred analytical methods for determining the value follow.

The Agency uses number-average molecular weight (NAVG MW) instead of the weight-average molecular weight (WAVG MW) for defining polymer exemption categories and criteria. The NAVG MW takes into account the number of molecules of various molecular weights in the polymer sample and therefore is representative of the average weight of the typical (major) components of a polymer sample. The WAVG MW takes into account the total weight of all molecules, placing no emphasis on the number of molecules at each individual weight. When the WAVG MW is calculated, a small percentage of large molecules can bias the average and give a false representation of the majority of molecules in the sample.

The equations for determining NAVG MW (M_n) and WAVG MW (M_w) are taken from the OECD guidelines draft proposal entitled "Determination of the Number-Average Molecular Weight and the Molecular Weight Distribution of Polymers using Gel Permeation Chromatography"³ and "Determination of the Low Molecular Weight Polymer Content."¹ In the equations, N_i is the number of molecules at a given molecular weight (which in gel permeation chromatography (GPC) is proportional to the detector signal for the retention volume V_i). M_i is the molecular weight of the polymer fraction at the retention volume V_i .

Equation 1:

$$M_n = \frac{\sum_i N_i}{\sum_i \frac{N_i}{M_i}}$$

Equation 2:

$$M_w = \frac{\sum_i (M_i N_i)}{\sum_i N_i}$$

Example 11:

The reason for using the NAVG MW instead of the WAVG MW in the criteria is best demonstrated by an example. Suppose a polymer contains 200 molecules that weigh 1,000 daltons, 300 molecules that weigh 1,500 daltons, 400 molecules that weigh 2,000 daltons and 2 molecules that weigh 1,000,000 daltons. In this case 99.8 percent of the molecules in this sample weigh \leq 2000 daltons. Clearly, one might say that typically, the polymer has a molecular weight from 1,000 to 2,000 daltons. The NAVG MW and the WAVG MW are calculated below:

$$M_n = \frac{902}{\frac{200}{1000} + \frac{300}{1500} + \frac{400}{2000} + \frac{2}{1,000,000}} = 1503$$

$$M_w = \frac{200,000 + 450,000 + 800,000 + 2,000,000}{902} = 3825$$

Of these two calculations, the M_n at 1503 daltons more accurately represents 99.8 percent of the molecules in the polymer batch. The M_w is biased by the two incidental 1,000,000 dalton molecules to the extent that the M_w average is a considerably greater weight than 99.8 percent of the sample.

The Agency requires that the manufacturer of an exempt polymer keep records of the "lowest" number-average molecular weight at which the polymer is to be made. This is not the value for the lowest MW species in a sample, but rather the lowest value of the NAVG MW obtained from polymer samples taken from a series of batches in the production of the polymer.

There are several analytical techniques for determining NAVG MW. Two literature references^{4,5} as well as OECD's guidelines document for testing of chemicals³ discuss methodologies in some detail and provide additional references. Brief summaries of the information provided in these references are given below. The techniques are based on molecular size (a function of the NAVG MW); colligative properties of polymer solutions (osmotic pressure, boiling point, freezing point, vapor pressure, etc.); or the number of chemically reactive groups present in the polymer. Any method that can be verified is acceptable for purposes of the polymer exemption. The following are most commonly used:

- Gel permeation chromatography (polymer size),
- Membrane osmometry (colligative property),
- Vapor-phase osmometry (colligative property),
- Vapor pressure lowering (colligative property),
- Ebulliometry (colligative property),
- Cryoscopy (colligative property), and
- End-group analysis (chemical reactivity).

5.1.1. GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC), the most frequently used and generally most reliable method for determining NAVG MW of polymers and oligomer content below 500 and 1000 daltons, is suitable for substances ranging from very low to very high molecular weights. In an ideal situation, separation of the polymer sample is governed by hydrodynamic radius (size) of each molecular species as it passes through a column filled with porous material, typically an organic gel. Smaller molecules penetrate the pores and thereby travel a longer path and elute after larger molecules. The GPC column must be calibrated using polymers of known weight and, ideally, similar structure. Polystyrenes are used quite extensively as internal standards. Detection techniques used for GPC are refractive index and UV-absorption.

One potential problem with GPC is band broadening, especially when measuring low molecular weight polymers, or as the result of unevenly packed columns or dead volumes. Empirical calibrations of the instrument can be made to minimize broadening⁶, but become unimportant when the ratio of the WAVG MW to the NAVG MW is greater than two. Another limitation with GPC is that many high molecular polymers are insoluble in usable solvents, and therefore can't be analyzed by GPC.

5.1.2. MEMBRANE OSMOMETRY

Membrane osmometry exploits the principle of osmosis for determining NAVG MW⁷. Polymer is placed in a membrane osmometer on one side of a semi-permeable membrane while a solvent is placed on the other. Solvent is drawn through the membrane as the system progresses toward equilibrium, creating a pressure differential that is dependent on the concentration difference and the molecular weight of the polymer.

The major disadvantage to this method is that accuracy and reliability may be compromised by diffusion of low weight oligomers through the membrane. Generally, diffusion is absent for unfractionated polymers with NAVG MWs greater than 50,000 daltons. The upper limit of the NAVG MW that may be measured with confidence is generally 200,000 daltons (OECD guidelines³).

5.1.3. VAPOR-PHASE OSMOMETRY

This method is based on the comparison of evaporation rates for a solvent aerosol and at least three other aerosols with varying polymer concentration in the same solvent. The technique is most accurate for polymers with NAVG MW less than 20,000 daltons (OECD guidelines³). This method is best applied to samples with molecular weight too low to be measured in a membrane osmometer.

5.1.4. VAPOR PRESSURE LOWERING

For this technique the basic principle is similar to vapor phase osmometry, however, vapor pressure is measured instead of the rate of aerosol evaporation. The vapor pressure of a reference solvent is compared against the vapor pressure of at least three concentrations of the polymer mixed with the solvent. Theoretically this technique may be applicable for polymers of up to 20,000 dalton NAVG Mws. In practice, however, it is of limited value.

5.1.5. EBULLIOMETRY

This technique exploits the boiling point elevation of a solution of a polymer to determine NAVG MW⁸. This method makes accurate determinations for polymers with NAVG MW approaching 30,000 daltons; however, it is limited by the tendency of polymer solutions to foam upon boiling. The polymer may even concentrate in the foam due to the foam's greater surface area, making the observed concentration of the polymer in solution less than the actual. It is customary to calibrate the ebulliometer with a substance of known molecular weight. Octacosane, with a molecular weight of 396 daltons, is a common choice.

5.1.6. CRYOSCOPY

Freezing point depressions of polymer solutions can also be used to determine NAVG MW. Although the limitations associated with cryoscopy are fewer than those of ebulliometry, care must be taken to avoid supercooling. The use of a nucleating agent to provide controlled crystallization of the solvent is helpful. Reliable results may be obtained for molecular weights of up to 30,000 daltons. As with ebulliometry, calibration with a substance of known molecular weight is customary.

5.1.7. END-GROUP ANALYSIS

This method is generally the least useful since a fair amount of prior knowledge, such as overall structure and the nature of the chain-terminating end groups, is needed about the polymer. Basically, end-group analysis methods take into account the number of molecules in a given weight of a sample, which in turn, yields the NAVG MW. End-group analysis is best suited to linear condensation polymers. For branched condensation polymers or addition polymers no general procedures can be established because of the variety and origin of the end-groups. However, when the polymerization kinetics are well known, the degree of branching may be estimated based on the amount of feedstock charged. For addition polymerization, end-group analysis can be used to determine molecular weight by analyzing for specific initiator fragments containing identifiable functional groups, elements, or radioactive atoms; for chain terminating groups arising from transfer reactions with solvent; or for unsaturated end groups such as in polyethylene and poly- α -olefins.

The analytical method used must distinguish the end groups from the main polymer skeleton. The most widely used methods are NMR, titration, or derivatization. For example, carboxyl groups in polyesters are usually titrated directly with a base in an alcoholic or phenolic solvent. Infrared spectroscopy is used when the polymer cannot be titrated due to insolubility in certain solvents. This technique is useful for NAVG MWs up to 50,000 daltons (with decreasing reliability as the NAVG is increased).

5.2. THE TWO PERCENT RULE AND CHEMICAL IDENTITY

According to the polymer exemption rule at §723.250(d)(4), a polymer is not eligible for exemption if it contains at greater than two weight percent monomers and/or reactants that are not: included on the TSCA Inventory, manufactured under an applicable TSCA §5 exemption, excluded from exemption, or an non-isolated intermediate. Monomers and reactants at greater than two percent make up the "chemical identity" of the polymer. For an exempt polymer, monomers and reactants at less than or equal to two weight percent are not considered part of the "chemical identity" of the polymer; and the use of these monomers and reactants creates a different set of issues, which are discussed below.

A manufacturer or importer must carefully decide at what weight percent level each monomer or other reactant is to be used in the preparation of the exempt polymer. This choice (which must be obvious from the manufacturing data kept by the manufacturer or importer) limits the manufacturer or importer of an exempt polymer in two major ways. First, if a certain monomer or reactant is used in an exempt polymer at less than or equal to two weight percent, the manufacturer may **not** later use that reactant at greater than two weight percent (under the exemption for the same polymer). The new polymer substance that results when the reactant is increased to greater than two weight percent is different, by definition, from the polymer that contains the reactant at less than or equal to two weight percent. Second, if a reactant or monomer is used at greater than two weight percent in an exempt polymer, the reactant or monomer must **not** be eliminated completely from the polymer (if the manufacturer is trying to satisfy the exemption for the same polymer). If either of these "identity-changing" events occur, the manufacturer must do one of the following: 1) find the new polymer identity on the TSCA Inventory, 2) submit a PMN at least 90 days prior to manufacture if the new polymer is not

on the Inventory, or 3) meet the conditions of a PMN exemption to cover the new polymer identity.

Non-Inventory monomers and reactants cannot be used in domestic manufacture (unless they are subject to another §5 exemption or are non-isolated intermediates). Therefore, a manufacturer cannot use such monomers and reactants for an exemption even at levels of two percent or less. A manufacturer will be able to exchange Inventory-listed monomers and reactants at less than or equal to two weight percent under one exemption, as long as such changes do not affect the eligibility of the polymer and records for such changes are maintained as stated in the rule. An exempt imported polymer under the new rule may contain non-Inventory monomers and reactants at two percent or less as long as they do not introduce into the polymer elements, properties, or groups that would render the polymer ineligible for the polymer exemption. The exception to this last statement is the **(e)(3)** type exempted polymer, for which monomers and reactants must only come from the **(e)(3)** list, even if at levels less than or equal to two percent. For all polymer types, restrictions unique to the polymer exemption must be applied in addition to the "Two Percent Rule."

Percent by weight has been defined as the weight of the monomer or other reactant used expressed as a percentage of the dry weight of polymer.

The Agency has long recognized that when calculating the percentage of each reactant, it is a matter of convenience rather than a matter of science to use the amount charged to the reactor, rather than the amount of a monomer incorporated into the polymer. EPA believes that the actual content of a polymer (what is actually incorporated into the polymer) is a better indicator of its physical, chemical, and toxicological properties, but has accepted calculations based upon the amount charged to the reaction vessel in order to facilitate PMN reporting for industry. Under the 1995 PMN rule revisions, the Agency now accepts two methods for determining the "percent by weight" of each reactant for the purpose of establishing the chemical identity of a polymer:

1). **The Percent Charged Method:** The percent composition of each monomer or reactant is established by the amounts charged to the reaction vessel.

2). **The Percent Incorporated Method:** The percent composition is based on the minimum theoretical amount of monomer or reactant needed to be charged to the reactor in order to account for the amount analytically determined to be incorporated in the polymer. The percent composition of each whole monomer or reactant whose fragment is present in the polymer should be established by analytical determination of the incorporated fragment, or may be established by theoretical calculations if it can be documented that an analytical determination cannot or need not be made to demonstrate compliance with the new polymer exemption rule.

At 40 CFR §723.250(g) the Agency specifies what identity information is required to be kept by the manufacturer or importer. By paragraph (1) of section (g), the Agency requires that a manufacturer or importer must identify, to the extent known or reasonably ascertainable, the specific chemical identity and CAS Registry Number (or EPA Accession Number) for each "reactant" used at any weight in the manufacture of an exempt polymer. This criterion is considered reasonable by the Agency based on the requirement that any reactant used at greater than two percent must already be listed on the TSCA Inventory or otherwise exempt under an appropriate §5 rule. There may be cases where a monomer or reactant was the subject of a previous PMN, exempted or excluded from exemption, hence the requirement to have a CAS registry number for such a monomer or reactant may not be necessary. However, manufacturers and importers should maintain in their records the CAS registry number for the monomer or reactant, if one exists for that substance).

At paragraph (2) of section (g), the Agency requests that a structural diagram be provided if possible, to further clarify the identity of an exempt polymer. The Agency believes it is possible to provide a representative

chemical structure diagram for nearly all polymers. It is often the structure that best illustrates the intended identity of a substance. For instance, if 2,2-bis(hydroxymethyl)propionic acid and an amine are among the feedstocks, would these two feedstocks react in such a way as to form amides or carboxylic acid salts? A structure makes clear the intent of the manufacturer or importer. All monomers and reactants at greater than two percent by weight in the polymer should be represented by the polymer structural diagram kept in the records.

5.2.1. PERCENT CHARGED METHOD

The calculations required to determine the percent by weight of a reactant charged to the reaction vessel are straightforward. The weight percent of the reactant is the weight of the material charged to the reactor (weighed before addition into the reaction), expressed as a percentage of the dry weight of the manufactured polymer (weighed after isolation from the reaction). The following equation applies, where 'GFC' is grams of feedstock charged, and 'GPF' is grams of dry polymer formed:

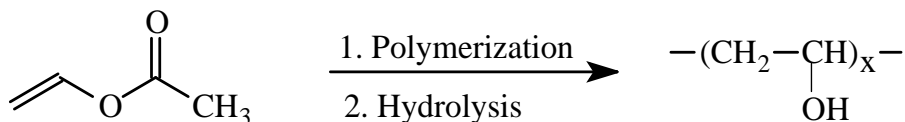
Equation 3:

$$\text{Percent by weight charged} = \frac{(GFC)}{(GPF)} \times 100$$

Calculations by percent charged to the reaction vessel can cause confusion if monomers or reactants lose a substantial portion of their molecular structure when incorporated into a polymer. Under these circumstances, the sum of the weights of reactants charged significantly exceeds, 100 percent. This type of calculation is demonstrated by Example 12, the formation of polyvinyl alcohol (PVA) produced from the polymerization of vinyl acetate followed by hydrolysis.

Example 12:

**Figure 6
Polyvinyl Alcohol and Weight Percent:**



The molecular weight of vinyl acetate is 86 daltons, and the molecular weight of the repeating unit for PVA [-CH₂-CH(OH)-] is 44 daltons. In this example, because only one monomer is used to form the polymer, and one monomer fragment is present in the polymer, the ratio of (GFC/GPF) is the same as (Feedstock MW/Fragment MW), so the equation can be simplified as follows:

$$\text{Wt. \% of vinyl acetate} = \frac{(86)}{(44)} \times 100 = 195$$

The weight percent of the vinyl acetate charged to the reactor is 195 percent!

5.2.2. PERCENT INCORPORATED METHOD

In the percent incorporated method, as stated in the 1995 PMN rule amendments, "the weight percent is based on...the minimum weight of monomer or other reactant required in theory to account for the actual weight of monomer or other reactant molecule or fragments chemically incorporated (chemically combined) in the polymeric substance manufactured." Therefore, if a percent incorporated is to be calculated for a monomer or reactant, the degree of incorporation of the fragment resulting from the monomer or reactant must be measured.

It is not always possible or feasible to determine analytically the degree of incorporation for every type of reactant, especially for random polymerizations where no repeating subunits exist and for polymerizations using chemical reactants where the structures are not completely specified (such a reactant as conjugated sunflower-oil fatty acids, for example). Complete or efficient incorporation cannot be assumed, even if the reaction equilibrium and kinetics predict a certain result. It is also necessary to identify a structural unit within the polymer that corresponds to the specific monomer from which it came. Often the same monomer unit may originate from more than one monomer. For example, empirically determining the exact chemical incorporation of oxirane, methyloxirane, ethylene diamine, and epichlorohydrin in a polymer would require a complicated study, perhaps using radioisotope-labeled reactants. If the percent incorporated cannot be deduced by measurement or reliably estimated, the manufacturer must use the percent charged method.

In order to calculate a weight percent incorporated for a reactant, certain data must be known: the molecular weight of the reactant charged; the molecular weight of the fragment that is incorporated into the polymer (if the feedstock is not entirely incorporated); and the analytically determined amount of the incorporated reactant that is present in the polymer (the weight percent of the polymer that consists of the fragment). From these data the number of moles of fragment present in the polymer can be calculated, which is proportional to the amount of feedstock that reacted to form the polymer. The following ratio is useful:

Equation 4:

$$\frac{\text{Wt. \% Frag.}}{\text{MW of Frag.}} = \frac{(\text{g Frag.})}{(100\text{g Polym.})} \times \frac{(\text{mol Frag.})}{(\text{g Frag.})} = \frac{\text{Moles of Frag.}}{100\text{g of Polym.}} = \text{Ratio A}$$

The weight percentage of reactant incorporated is calculated by converting moles of incorporated fragment per 100 g of polymer (Ratio A), to moles of reactant and then multiplying by the reactant molecular weight. (The specific units used are irrelevant; gram-moles per 100 grams or ton-moles per 100 tons are equally valid for the calculation.) This is accomplished by the following equation:

Equation 5:

$$\text{Wt. \% React. Incorp.} = (\text{Ratio A}) \times \frac{(\text{Moles React.})}{(\text{Moles Frag.})} \times (\text{MW of Reactant}) \times 100$$

Example 13:

For an example of the calculation for the percent incorporated method consider the polymerization of ethylene glycol with a dialkyl terephthalate. It is known that both oxygen atoms of the glycol are incorporated into the resulting polyester while two alkoxy groups of the terephthalate ester are lost in the process. The following calculation determines the weight

percentage incorporated for dialkyl terephthalate: The polymer was empirically shown to contain 13.2 percent by weight of the terephthaloyl unit $[-C(=O)-C_6H_4-C(=O)-]$, which has a MW of 132 daltons. Ratio A for terephthaloyl is calculated as follows:

$$\text{Ratio A} = \frac{(13.2 \text{ g})}{(100 \text{ g polymer})} \times \frac{(1 \text{ mole})}{(132 \text{ g})} = \frac{(0.10 \text{ moles terephthaloyl})}{(100 \text{ g polymer})}$$

The weight percent of reactant incorporated is calculated as shown below. Each mole of parent dialkyl terephthalate ester would result in one mole of fragment, so the molar conversion factor is 1. If the dialkyl terephthalate charged is dimethyl terephthalate, the MW used for the calculation is 194 g/mole.

$$\text{Wt. \% React. Incorp.} = \frac{(0.10 \text{ moles})}{(100 \text{ g Polymer})} \times \frac{(1 \text{ mole of Feedstock})}{(1 \text{ mole of Fragment})} \times 194 \times 100 = 19.4$$

Example 14:

For a comparison to Example 13, consider if the dialkyl terephthalate charged were diethyl terephthalate. The MW for the diethyl terephthalate is 222 g/mole. The calculation would show a weight percent of reactant incorporated as 22.2 percent. This would mean that diethyl terephthalate would have to be charged to the reaction vessel at 22.2 percent for the terephthaloyl fragment to be incorporated into the polymer at 13.2 percent; whereas dimethyl terephthalate would have to be charged at only 19.4 percent to have the terephthaloyl fragment incorporated at 13.2 percent. These percentage values make sense because a larger alkoxy group is lost when the diethyl terephthalate is the source of the terephthaloyl group than when dimethyl terephthalate is the source of the terephthaloyl groups and the methoxy group is lost. Therefore, to provide the same fragment incorporated in the polymer, more weight of diethyl terephthalate would have to be charged in comparison to dimethyl terephthalate.

Example 15:

Neutralizers are often used in considerable excess over the amount actually incorporated into the polymer. If the amount of incorporation is two percent or less, neutralizer may be omitted from the identity of the polymer. A sample calculation of the "weight percent incorporated" for a neutralizing base is given below:

A polymer containing free carboxylic acid functional groups was neutralized using a large excess of sodium hydroxide (NaOH; formula weight = 40); the total amount of base charged to the reactor was 10 percent. Analysis of the resulting polymer salt revealed that the polymer contained 0.92 weight percent of sodium (atomic weight = 23), coming only from the base. This amount of sodium corresponds to 0.04 moles of sodium per hundred grams of polymer, or 1.6 grams of NaOH per hundred grams of polymer -- that is, 1.6 weight percent NaOH incorporated, despite the large excess charged. Because the weight percent of NaOH is not greater than two percent, the polymer substance would not have to be described as the sodium salt.

$$\text{Ratio A for Na} = \frac{(0.92 \text{ g Na})}{(100 \text{ g Polym.})} \times \frac{(1 \text{ mol Na})}{(23 \text{ g Na})} = \frac{(0.04 \text{ moles Na})}{(100 \text{ g Polym.})}$$

$$\text{Wt. \% Inc. NaOH} = \frac{(0.04 \text{ mol Na})}{(100 \text{ g Polym.})} \times \frac{(40 \text{ g NaOH})}{(1 \text{ mol NaOH})} \times 100 = 1.6$$

If sodium bicarbonate (NaHCO_3 ; formula weight = 86) had been the neutralizing agent, the same number of moles of sodium per hundred grams of polymer would have corresponded to 3.36 weight percent of NaHCO_3 . Because the weight percent of NaHCO_3 is greater than two percent, the polymer substance must be described as the sodium salt.

$$\text{Wt. \% Inc. NaHCO}_3 = \frac{(0.04 \text{ mol Na})}{(100 \text{ g Polym.})} \times \frac{(84 \text{ g NaHCO}_3)}{(1 \text{ mol NaHCO}_3)} \times 100 = 3.36$$

If a combination of bases is used for neutralization, the amounts incorporated should be prorated according to the mole ratios of the neutralizing agents charged if the reactivities are similar. Otherwise, assume the most reactive neutralizing agents is consumed first, etc.

Example 16:

For calculating the weight percent incorporated of an initiator, the computation will be similar to that for an excess neutralizing base. Initiator may be charged to the reaction vessel at a higher percentage than what is actually incorporated into the polymer. If the amount of incorporation is consistently below two percent, the initiator will not be in the chemical identity of an exempted polymer. (For polymers with PMNs and NOCs, the submitter has the option of leaving the initiator out of the identity, or including it.) In the case where initiator is not in the identity of the either an exempted polymer or in the identity of a polymer covered by a PMN and NOC, a change in initiator could be made without having to establish another polymer exemption or PMN for the change in the polymer manufacture, as long as the alternate initiator remained at or under two percent and in the case of the exemption, the initiator did not exclude the polymer in other ways. A sample calculation of the "weight percent incorporated" for an initiator is given below:

A polyolefin with a NAVG MW of 9,000 daltons was produced using azobis[isobutyronitrile] (AIBN, MW = 164) charged at 3 percent. This class of initiator is known to produce radicals that contain the nitrile moiety (CN, FW = 26), which can be analytically determined. The polymer sample was found to contain 0.29 weight percent nitrile, which was assumed to originate only from AIBN. This 0.29 g of fragment in 100 g of polymer corresponds to 0.011 moles of fragment $[(0.29 \text{ g} / 26 \text{ g/mol}) = 0.011 \text{ moles}]$ in 100 g of polymer. Since every 1 mole of AIBN reactant produces 2 moles of fragment, a molar conversion factor of 1/2 is used to relate the amount of fragment present to the amount of reactant incorporated. The weight percent of reactant incorporated is calculated as follows:

$$\text{Wt. \% React. Inc.} = (\text{Ratio A}) \times \frac{(\text{Moles of React.})}{(\text{Moles of Frag.})} \times (\text{MW of React.}) \times (100)$$

or

$$\text{Wt. \% AIBN Incorp.} = \frac{(0.011 \text{ moles Frag.})}{(100 \text{g Polym.})} \times \frac{(1 \text{ Mole React.})}{(2 \text{ Moles Frag.})} \times (164) (100) = 0.9$$

As stated at the beginning of this example, AIBN was charged to the reaction vessel at 3 weight percent, but only 0.9 percent was actually incorporated into the polymer. After establishing that the weight percent of AIBN incorporated is less than or equal to two percent, the submitter need not include it in the polymer identity.

5.2.3. METHODS FOR DETECTION OF POLYMER COMPOSITION

There are many methods available for chemical analysis of polymers and for detecting weight percent of fragments incorporated. Although any analytical method that can be verified is acceptable, this section explores some of the more common approaches. The following list of options is not meant to be exhaustive:

- Classical chemical analysis (elemental analysis, titration, etc.),
- Mass spectrometry,
- Gas chromatography,
- Infrared spectroscopy,
- Nuclear magnetic resonance spectroscopy, and
- X-ray diffraction analysis.

A brief description for each of the non-chemical methods of analysis follows.

5.2.3.1. MASS SPECTROMETRY

In mass spectrometry, an electron beam bombards a sample and creates from it positive ion fragments that are separated by mass to charge ratio in an electromagnetic field and measured quantitatively. From the abundance of the various ionic species found, the structure and composition of the original substance can be inferred. When mass spectrometry is used for analyzing polymers, the polymer is usually thermally degraded first to form fragments of low molecular weight. These fragments are volatilized, ionized and then separated as per the standard technique.

5.2.3.2. GAS CHROMATOGRAPHY

In gas chromatography (GC) gaseous or vaporized components of the sample are distributed between a moving gas phase and a fixed liquid phase or solid absorbent. By a continuous succession of elution steps, occurring at different rates for each species, separation is achieved. In the resulting gas chromatogram the peaks are proportional to the instantaneous concentration of the components. Therefore, information about the number, nature, and weight percentages of the components can be derived.

5.2.3.3. INFRARED SPECTROSCOPY

Infrared frequencies are in the wavelength range of 1 to 50 microns and are associated with molecular vibration and vibration-rotation spectra. Often for polymers, the infrared absorption spectra are surprisingly simple. This is because many of the normal vibrations have the same frequency and the strict selection rules for absorption prevent many of the vibrations from causing absorption peaks in the spectrum. Rarely can infrared be used for quantitative analysis of polymer composition.

5.2.3.4. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool in the study of chain configuration, sequence distribution, and microstructures in polymers. NMR spectroscopy utilizes the property of spin angular momentum possessed by nuclei whose atomic number and mass number are not both even. Irradiation of the sample by a strong magnetic field splits the energy level into two: one corresponding to alignment of electrons with the field and the other with an antiparallel alignment. Transitions between these states lead to spectra. Peak intensity is proportional to concentration for proton NMR.

5.2.3.5. X-RAY DIFFRACTION ANALYSIS

X-ray diffraction is a useful method for detecting the presence of structures that are arranged in an orderly array or lattice. The interferences that result from the lattice interaction with electromagnetic radiation provides information regarding the geometry of the structures. Since single crystals of polymer as now prepared are too small for x-ray diffraction experiments, the crystal structure is generally derived from a fiber drawn from the polymer.

5.3. CALCULATING FUNCTIONAL GROUP EQUIVALENT WEIGHT

Reactive functional groups that come from monomers and reactants at greater than or equal to two percent in a polymer must meet the minimum FGEW requirements for the exemption category under which the polymer is manufactured or imported. Polymers that are exempt under the (e)(1) criteria must meet or exceed the minimum permissible equivalent weights for reactive functional groups (FGEW). There are no functional group restrictions for polymers meeting the (e)(2) exemption except for cationic and potentially cationic group concerns, as specified in §723.250(d). For (e)(3) polymers, reactive functional groups of moderate and high concern would not be present in any polymer derived from monomers on the allowed list. In addition, the monomers on the list are not expected to bear reactive functional groups of moderate or high concern once they are incorporated into the polymer. Hence, the (e)(3) section of the new polymer exemption rule does not have any FGEW requirements.

For (e)(1) polymers the allowable thresholds for certain reactive functional groups are listed in the Table 4. Note: this is not an exhaustive list. Consult the 1995 polymer exemption rule for groups not mentioned. Note that if a functional group is not mentioned in the rule among the low-(e)(1)(ii)(A) or moderate-concern groups (e)(1)(ii)(B), it is considered to be a high-concern functional group. Low-concern reactive groups may be used without limit, and no thresholds have been set for them.

Table 4
Allowable Thresholds for Reactive Functional Groups

Moderate-Concern: The minimum permissible FGEW is 1,000 daltons.

Acid halides
Acid anhydrides
Aldehydes
Alkoxysilanes where alkyl is greater than C2
Allyl ethers
Conjugated olefins
Cyanates
Epoxides
Hemiacetals
Hydroxymethylamides
Imines
Methylolamides
Methylolamines
Methylolureas
Unsubstituted position ortho- or para- to phenolic hydroxyl

High-Concern: The minimum permissible FGEW is 5,000 daltons.*

Acrylates
Alkoxysilanes where alkyl = methyl or ethyl
Amines
Aziridines
Carbodiimides
Halosilanes
Hydrazines
Isocyanates
Isothiocyanates
.alpha.-Lactones; .beta.-Lactones
Methacrylates
Vinyl sulfones

* For polymers containing high-concern functional groups, the FGEW_{combined} must be greater than or equal to 5,000 daltons taking into account high-concern (e)(1)(ii)(c) and, if present, moderate-concern (e)(1)(ii)(b) functional groups.

Unless a functional group equivalent weight can be determined empirically by recognized, scientific methodology (typically titration), a worst-case estimate must be made for the FGEW, in which all moderate- and high-concern functional moieties must be factored. A generalized approach for performing equivalent weight estimations with specific methods and examples is provided below. The following is limited guidance on how to calculate functional group equivalent weights. The methods discussed are end-group analysis (Section 5.3.1), calculation based on percent charged (Section 5.3.2.), and nomograph use (Section 5.3.3.).

5.3.1. END-GROUP ANALYSIS

Most condensation polymers (polyesters, polyamides, etc.) contain reactive functional groups only at the chain ends, because all other reactive functionality in the monomers is consumed to produce the condensation polymer backbone in the final product. For this type of polymer, FGEW determination may be as simple as theoretical end group analysis and can be performed regardless of the reactive group type.

For a linear polymer (two reactive groups per monomer) with either the nucleophilic or electrophilic reagents in excess, the FGEW is half the NAVG MW, as described.

EXAMPLE 17:

A polyamide with a NAVG MW of 1000 daltons, made from excess ethylene diamine (two nucleophiles) and adipic acid (two electrophiles), would be anticipated to be amine-terminated at both ends, assuming a worst case scenario (the greatest content of reactive functional groups present). The amine equivalent weight would be 1/2 the NAVG molecular weight, or 500 daltons.

For simple, branched condensation polymers (having only one monomer possessing more than 2 reactive sites), the FGEW must be calculated from the total number of end groups present in the polymer. This is calculated from an estimated degree of branching, which is derived by knowing the number of reactive groups in the polyfunctional monomer. If reasonable, it should be assumed that the monomer responsible for the branching will be incorporated in its entirety to form the polymer.

The mathematics for estimating the FGEW for simple branched condensation polymers follows. The equivalent weight of the monomer is the molecular weight of the monomer divided by the weight percent charged to the reaction vessel. The monomer equivalent weight of 1000 daltons means that there is one mole of monomer for every 1000 daltons of polymer.

Equation 6:

$$\text{Monomer Equivalent Wt.} = \frac{(\text{Monomer molecular weight})}{(\text{Weight Percent Charged})}$$

The degree of branching is calculated by dividing the NAVG MW value by the monomer equivalent weight, multiplied by the number of reactive groups that are not used to make the polymer backbone, which is (NRG - 2). (The NRG value is the number of reactive groups originally in the monomer.)

Equation 7:

$$\text{Degree of Branching} = \frac{(\text{NAVG MW})}{(\text{Monomer Eq. Wt.})} \times (\text{NRG}-2)$$

The total number of end-groups in the polymer is the degree of branching value plus two, where the two in this equation is the number of end-groups of the polymer backbone.

Equation 8:

$$\text{Total number of Polymer End Groups} = \text{Degree of Branching} + 2$$

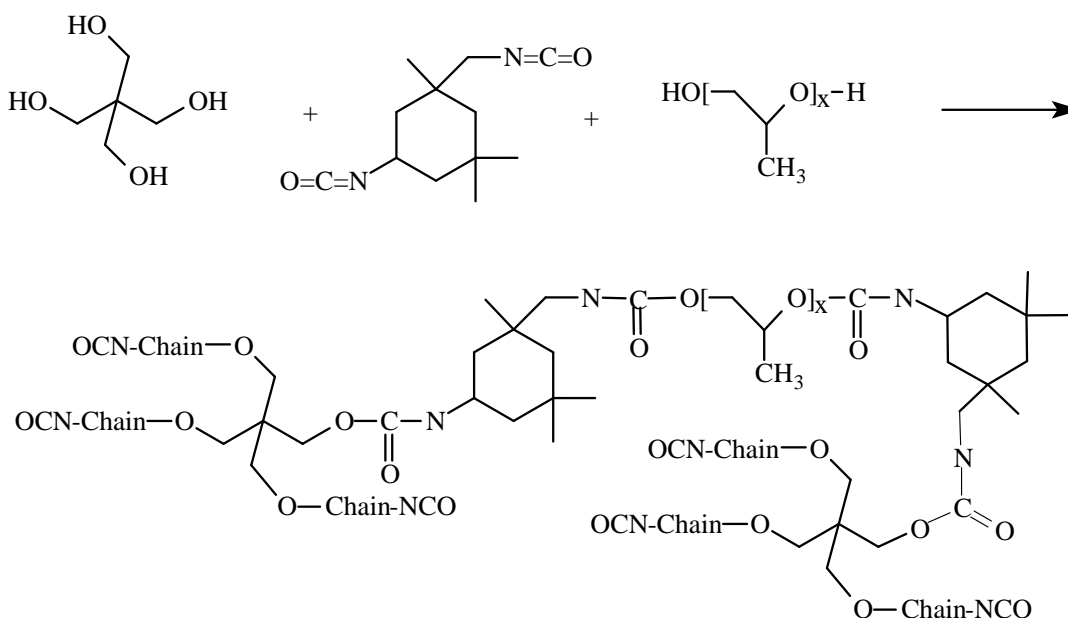
The FGEW is then derived by simply dividing the NAVG MW by the number of end-groups in the polymer.

Example 18:

Consider the polymerization of pentaerythritol (PE, 4 reactive groups) with polypropylene glycol (PPG, 2 reactive groups) and an excess of isophorone diisocyanate (2 reactive groups). The polyfunctional feedstock (PE) is added to the reaction at 10 percent by weight to produce an isocyanate-terminated polymer having a NAVG molecular weight equal to 2720 daltons. The monomer

equivalent weight of pentaerythritol is 1360, obtained by dividing the monomer molecular weight by the weight percent charged ($136 \div 0.10$). PE has four reactive alcohol moieties, two are used to form the polymer backbone and the other two form branches. Following the equations given above, the degree of branching for this polymer example is $[(2720 \div 1360) \times (4 - 2)] = 4$. The total number of end-groups is $[4 + 2] = 6$. Due to the excess of isophorone diisocyanate, we assume that each end-group is an isocyanate group. Finally, the FGEW can be calculated by simply dividing the NAVG MW by the total number of end groups theoretically present. Therefore, $FGEW = (2720 \div 6) = 453$ daltons.

Figure 7
Isocyanate-Terminated Urethane and Functional Group Equivalent Weight:



For condensation polymers derived from a more complex mixture of feedstocks, computer programs that simplify the complicated FGEW calculations may be used. (There are a few commercial programs which perform a "Monte Carlo" simulation of a random condensation polymerization that directly estimates the NAVG MW and FGEW from the types of data described earlier.) Analytical data should be used periodically to confirm computer estimates and verify eligibility.

5.3.2. MORE COMPLEX FGEW CALCULATIONS

Some condensation and addition reactions create polymers where not all reactive functional groups along the backbone of the polymer are consumed during the reaction, so a simple end-group analysis will not suffice for determining an accurate FGEW. In many of these cases the equations in this section may be used to estimate FGEWs. These equations aid in calculating FGEWs for elements (for example, basic nitrogen), for reactive groups that are unchanged under the reaction conditions and for multiple types of functional groups that remain in the polymer molecule.

Equation 9 can be used for any reactive functional group in a polymer. This may even be an atom, such as basic nitrogen, as in an example that follows. In the equation, 'FWG' is the formula weight of the group; and 'W%G' is the weight percent of the group:

Equation 9:

$$FGEW = \frac{(FWG) \times 100}{(W\%G)}$$

Example 19:

To calculate the amine FGEW for a polymer containing 2.8 weight percent basic nitrogen (using 14.0, the atomic weight of nitrogen, as the formula weight of the group), the equation becomes:

$$FGEW = \frac{14.0 \times 100}{2.8} = 500$$

Functional groups are typically introduced into polymers from the precursor monomers. Using Equation 10 one may calculate the weight percent of the functional group in the polymer, as long as the monomer is included in its entirety and the functional groups are introduced unchanged. In Equation 10, 'FWG' is formula weight of the group, 'NGM' is the number of groups in the monomer, 'W%M' is the weight percent of the monomer, and 'FWM' is the formula weight of the monomer:

Equation 10:

$$\text{Weight \% of Group} = \frac{(FWG) \times (NGM) \times (W\%M)}{(FWM)}$$

Substituting Equation 10 into Equation 9, FGEW Equation 11 is obtained, where 'FWM' is the formula weight of the monomer, 'W%M' is the weight percent of the monomer, and 'NGM' is the number of groups in the monomer:

Equation 11:

$$FGEW = \frac{(FWM) \times 100}{(W\%M) \times (NGM)}$$

Example 20:

For an acrylic polymer containing 5.4 weight percent of acryloyl chloride (formula weight 90.5) as a monomer, the FGEW of acid chloride groups in the polymer is:

$$FGEW = \frac{(90.5)(100)}{(5.4)(1)} = 1676$$

If the various moderate- and high-concern functional groups in the polymer arise from more than a single monomer, the $FGEW_{\text{combined}}$ may be calculated using Equation 12. Also, if several different monomers contain the same groups, for example, if three monomers contribute epoxides which remain intact in the polymer, Equation 12 may be used to calculate the epoxide FGEW. This combined epoxide FGEW should be compared to the minimum permissible FGEW for epoxides when determining eligibility of the polymer.

In Equation 12, $FGEW_n$ is the FGEW for each particular functional group in the polymer:

Equation 12:

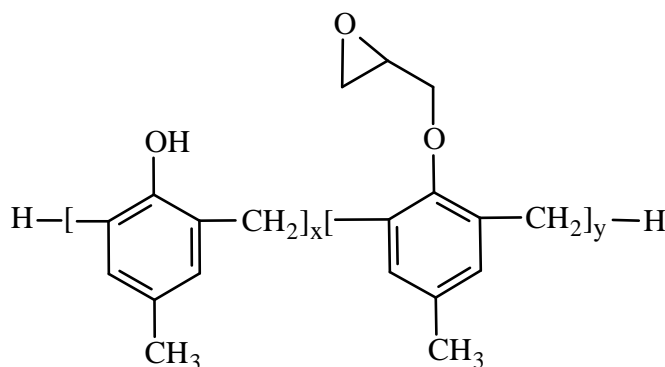
$$FGEW_{combined} = \frac{1}{\frac{1}{FGEW_1} + \frac{1}{FGEW_2} + \dots + \frac{1}{FGEW_n}}$$

Example 21:

This calculation of FGEW demonstrates the use of end-group analysis and equation estimations.

Some condensation polymers contain unreacted reactive functional groups in addition to the end groups of interest; for example, an epoxide-capped phenol-formaldehyde novolak resin. The FGEW for each type of reactive group present in the molecule (end groups and unreacted groups) should be calculated separately and then summed using Equation 12. Assume a para-cresol and formaldehyde copolymerization produced a condensation polymer that was reacted with one percent epichlorohydrin. The NAVG MW of this product was determined

Figure 8
Epoxide-capped Novolak and Functional Group Equivalent Weight:



by GPC to be 8,000 daltons. It would be difficult to show empirically that the polymer would not be phenol-terminated. Therefore, the polymer is assumed to be phenol-terminated as a worst case scenario. This would mean phenol groups with reactive ortho positions reside at the polymer backbone termini. The FGEW for the terminal phenolic ortho positions is (NAVG MW / 2), or 4,000 daltons. This is above the minimum permissible functional group equivalent weight for the phenol reactive group which is of moderate concern (1000 daltons minimum permissible weight). If the terminals are the only reactive groups in the polymer, this polymer would be eligible for exemption. However, epoxy rings from the epichlorohydrin are also present, so the FGEW for epoxide must also be considered. Even though epichlorohydrin would not be included in the chemical identity of the polymer being considered for exemption, (it is charged at less than two percent by weight), the FGEW for the epoxide must be included for the FGEW_{combined} calculation. Following Equation 11, the epoxide FGEW is calculated to be 9,250. (The molecular weight for epichlorohydrin, 92.5 was used; along with 1 percent for the amount charged, and 1 as the number of reactive epoxides.) The FGEW of 9,250 means that there is one epoxide moiety present for every 9,250 daltons of polymer. If epoxide were the only reactive group in the polymer the minimum equivalent weight requirement for moderate concern groups would be exceeded and the polymer would meet the FGEW criteria for exemption. However, for a polymer with more than one type of reactive group of concern, a FGEW_{combined} must be calculated to determine exemption eligibility.

For the polymer, the phenolic FGEW is 4,000 and for epoxides the FGEW is 9,250. The FGEW_{combined} would be calculated following Equation 12, as follows:

$$FGEW_{combined} = \frac{1}{\frac{1}{4000} + \frac{1}{9250}} = 2792$$

With a $FGEW_{combined}$ of 2,792 daltons, this polymer would be eligible for exemption because the $FGEW_{combined}$ is greater than the required 1,000 minimum permissible equivalent weight (threshold level). Although there are two reactive functional groups from the moderate-concern list, there are no high-concern groups present.

However, note that if instead of epichlorohydrin, 1 percent of acryloyl chloride (high-concern reactant with a molecular weight 90.5) had been used, the same type of calculation would produce a polymer that is excluded from the exemption. In this further example, groups from (e)(1)(ii)(B) and (e)(1)(ii)(C) are both present and give a $FGEW_{combined}$ of 2,774 daltons. The threshold of 5,000 daltons is not satisfied.

$$FGEW_{combined} = \frac{1}{\frac{1}{4000} + \frac{1}{9050}} = 2774$$

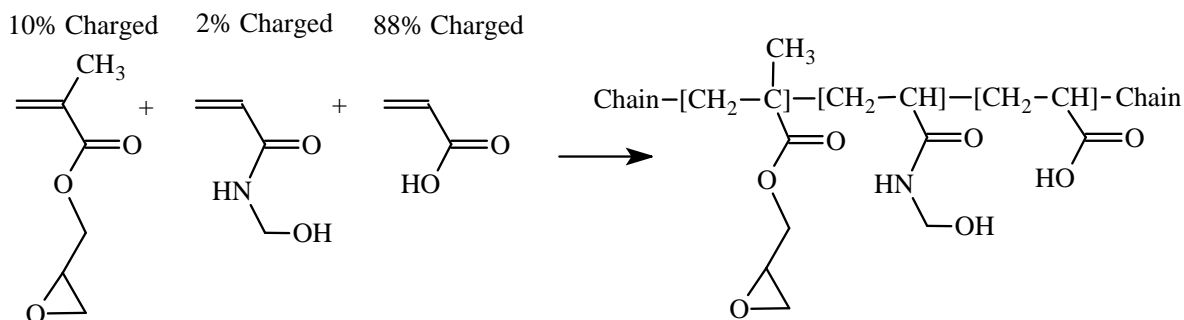
Example 22:

Similar calculations may be done for addition reaction polymers. Consider a radical polymerization of acrylates, which react via the alkene leaving reactive functionality in the molecule. In this case it would be reasonable to assume that each monomer charged to the reaction vessel will be incorporated in its entirety to form polymer.

Assume that polyacrylate was produced from 10 percent glycidyl methacrylate (MW = 142), two percent hydroxymethyl acrylamide (MW = 101) and 88 percent acrylic acid. (See Figure 9). The reactive functional groups of concern are the epoxide (1,000 dalton threshold) from glycidyl methacrylate and the hydroxymethyl amide from the acrylamide (1,000 dalton threshold). The carboxylic acid moiety from acrylic acid may be used without limit. (See the rule, section (e)(1)(A); and also the tables in this manual.)

Using Equation 11, one can calculate the FGEW for the epoxide to be 1,420 daltons (142 / 0.10), and the FGEW for hydroxymethyl amide to be 5,050 daltons (101 / 0.02). (If either of these monomers had been used separately in the stated proportions, the polymer FGEW eligibility restrictions would have been met.) The $FGEW_{combined}$ for the polymer calculated using Equation 12 is 1,108 daltons ($1 / [(1/1420) + (1/5050)]$). This polymer would be eligible for the exemption because the 1,000 dalton threshold for two or more moderate-concern reactants was met. Because 1,108 daltons is fairly close to the 1,000 dalton threshold, the manufacturer will not have a lot of flexibility to increase the epoxide or amide in future batches. Also, each batch must meet the exemption. If it is anticipated that some batches will not qualify for the exemption, the manufacturer or importer must file a regular PMN 90 days prior to the manufacture of the commercial product, to cover those particular production runs.

Figure 9
Acrylate with Multiple Functional Groups:



In some addition reactions the reactive groups that effect the desired polymerization reaction are consumed and in others they are not. Examples 23 and 24 contrast these two types.

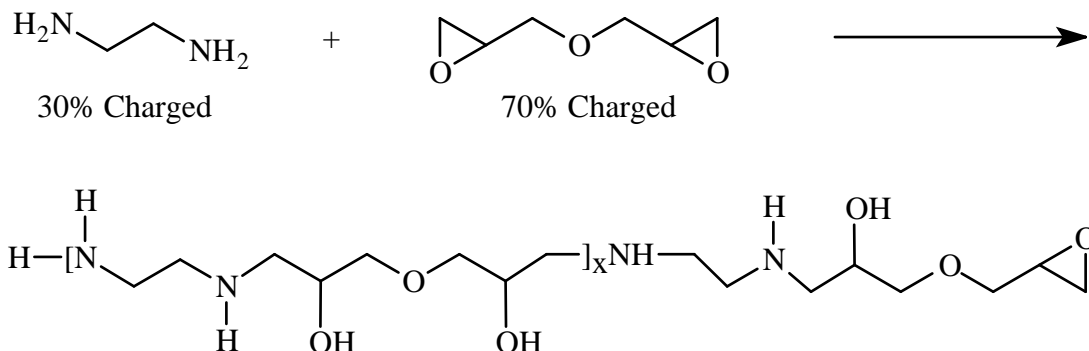
Example 23:

An example of an addition reaction that consumes the reactive functional groups is the addition of an amine to an isocyanate molecule. The reactive amine adds to the isocyanate to produce a "urea" polymeric backbone which is unreactive. Typically, an end-group analysis would be used to determine if the FGEW falls within the allowable limits for the exemption.

Example 24:

An addition reaction where the reactive group involved in the polymerization is not consumed (is still considered reactive) involves a more complicated calculation of FGEW.

Figure 10
Unconsumed Amines and Combined Functional Group Equivalent Weight:



Consider the reaction between ethanediamine (MW = 60) charged at 30 percent, and diglycidyl ether (MW = 130) charged at 70 percent. In the reaction, amine nitrogens react with the epoxides. This results in consumption of the epoxide to form an aliphatic alcohol, which is on the low-concern list and may be present in any quantity. The amine functionality remains intact and the FGEW

for the amine is proportional to the amount of feedstock containing the amine charged to the reaction vessel. The FGEW for the amines in this type of reaction is estimated using Equation 11, the molecular weight of the feedstock (60), the percent of the monomer charged to the reaction vessel (30), and the number of reactive functional groups in the feedstock (2):

$$FGEW = \frac{60 \times 100}{30 \times 2} = 100$$

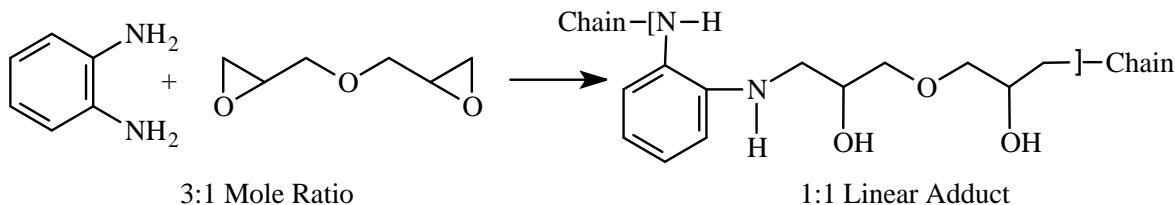
The minimum permissible equivalent weight for amines is 5,000 daltons. Because adding more groups to the $FGEW_{combined}$ calculation can only lower the value, no further calculation would be necessary since the polymer would not be eligible by amine content alone. This is demonstrated by factoring in the epoxide contribution. The polymer would likely be epoxide-terminated because of the excess molar amount of glycidyl ether charged. If this polymer had a NAVG MW = 5,000 daltons, the epoxide FGEW would be 2,500 daltons by end group analysis, assuming linear polymerization. The epoxide-terminated polymer containing reactive amines would have a $FGEW_{combined}$ equal to 96 daltons $[1 \div [(1/100) + (1/2500)]]$.

In some addition polymer processes one reactant (or group of reactants) is used in large excess compared to the other reactants. The reporting of residual amounts of monomers or other reactants is not required under the new rule. (The amount of reactant that does not form polymer is not regulated by the new polymer exemption rule, since these residual, unreacted materials must be on the TSCA inventory and are covered by different Agency authority, as existing chemicals.) For polymers made under these conditions, a simple repeating unit of known molecular weight can be assumed. The FGEW can be calculated by dividing the unit molecular weight by the number of groups in the unit.

Example 25:

A polyamine was made from the addition of 70 weight percent 1,2-benzenediamine (MW = 108) to 30 weight percent of diglycidyl ether (MW = 130). The diamine:diepoxide ratio equals about 3:1, as charged to the reaction vessel. A linear polymer of a 1:1 adduct (MW = 238) is the most likely

Figure 11
Repeating Units, A Polyamine and Functional Group Equivalent Weight:



representative repeating unit. The amine FGEW would be 119 daltons (the repeating unit MW of 238 daltons divided by two, the number of reactive amines in the repeating unit). The FGEW will not change regardless of the number of repeating units in the polymer or the amount of excess diamine monomer.

5.3.3. DETERMINING FGEW BY NOMOGRAPH

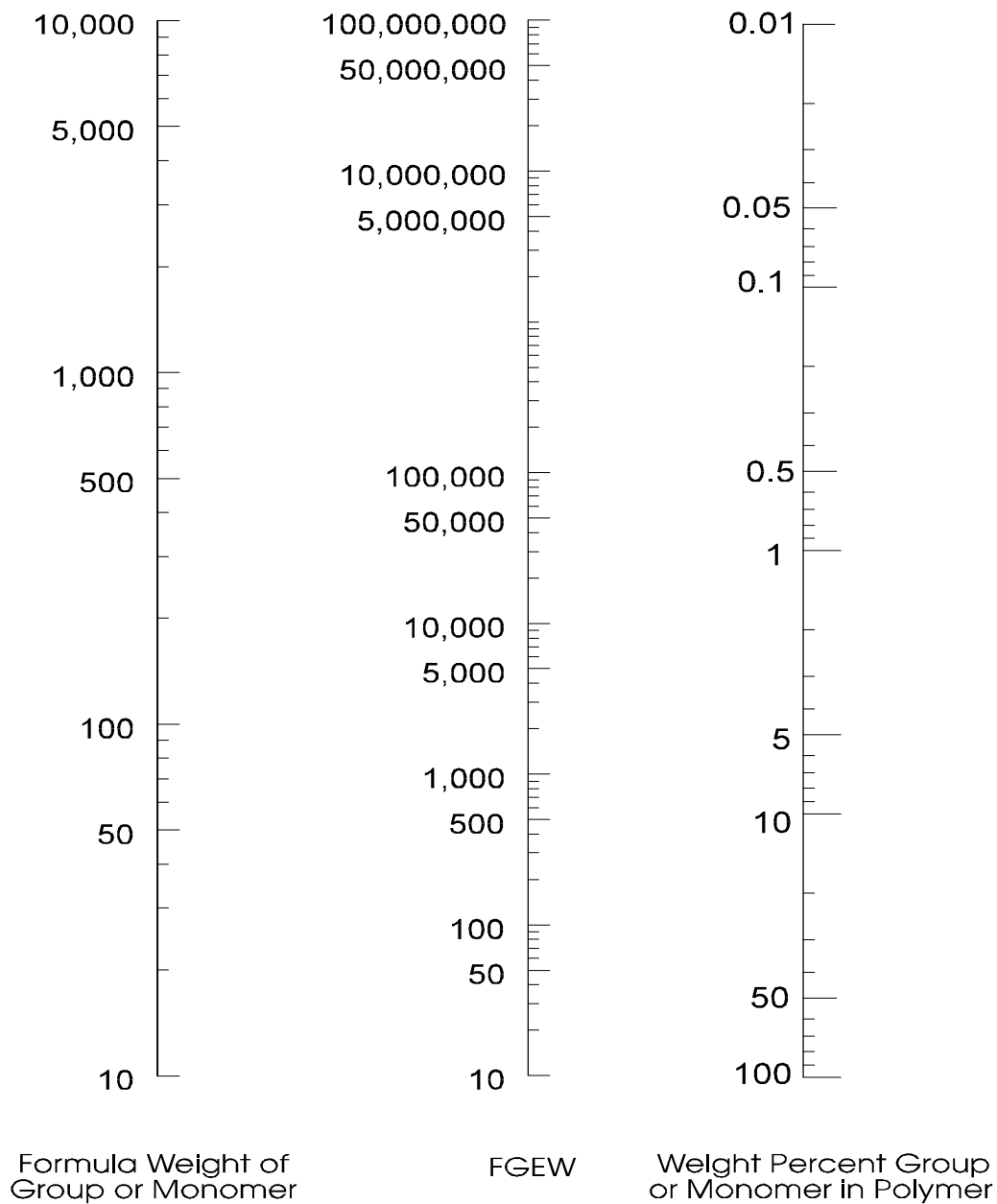
The nomograph in Figure 12 has been developed to aid in the estimation of FGEW. The logarithmic axes on the nomograph are "Formula weight of group or monomer," "FGEW," and "Weight percent of group or monomer in the polymer." Choosing the axis points for the first and last of these data and drawing a line between the two points will intersect the FGEW axis at the point representing the FGEW for the monomer or group being estimated. For monomers containing several identical groups, the FGEW should be divided by the number of identical groups in the monomer. For the case of several different monomers containing the same groups use FGEW equation 4 instead of the nomograph.

6. OTHER REGULATIONS AND REQUIREMENTS

Please consult the new rule at 60 FR 16316-16336 (USEPA 1995) for any of the following topics:

- Exemption Report and Requirements
- Chemical Identity Information
- Certification
- Exemptions Granted Under Superseded Regulations
- Recordkeeping
- Inspections
- Submission Information
- Compliance
- Inspections
- Confidentiality

Figure 12
Nomograph for Determining FGEW



7. COMMON QUESTIONS AND ANSWERS

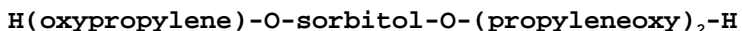
POLYMER DEFINITION:

1. In determining whether a polymer is on the Inventory, does the "new" polymer definition under the polymer exemption apply? For example, if I manufacture a substance of the type $R(OCH_2CH_2)_nOSO_3Na$ where $n =$ an average of 7, will I have to submit a PMN even though >3 units of consecutive monomer are present? The Inventory currently considers all the ethoxylates with >3 units as polymeric, and therefore as the same substance. What if $n =$ exactly 7? Exactly 15?

The alkyl ethoxylate sulfates with definite numbers of repeating units that you describe would not meet the polymer definition, because they would consist of molecules of a single molecular weight. Chemical Abstracts nomenclature rules and the TSCA Inventory nevertheless does treat some of these as though they were polymers. For example, "laureth sulfate", which corresponds to the formula above where $R = C_{12}H_{25}$ and $n = x$, is on the Inventory (CASRN 9004-82-4). Variations in the number of ethylene oxide units, as long as n is either >10 or variable or represents an average value, will not produce a new (that is, non-Inventory) substance. Thus laureth sulfate with n averaging 7 is considered an existing substance, as is laureth sulfate with $n =$ exactly 15. However, the case where $n =$ exactly 7 is considered a discrete chemical substance, not a polymer, and would not be considered the same. It would have a different name and CASRN, and would be a new chemical if it is not already on the Inventory elsewhere. This has always been true, and is unchanged by the polymer exemption.

The "new" polymer definition does not affect the Inventory status of existing polymers or of new polymers submitted under the PMN rule. The polymer definition, which applies only to polymers manufactured under the polymer exemption, therefore does not have the effect of creating a set of "no longer polymers".

2. Would the following example count as a "polymer molecule?" (The longest straight chain is $1+1+2=3+1$.)



No. Sorbitol cannot be a repeating unit under the conditions of the relevant polymerization reaction (propoxylation), so it is considered an "other reactant". Therefore the longest sequence of monomer units (considered as derived from propylene oxide) is two. A continuous string of at least three monomer units is required, plus one additional monomer unit or other reactant.

3. How do you apply the molecular weight distribution requirement of the polymer definition (i.e., <50 percent of any one MW) to highly cross-linked polymers of essentially infinite MW?

For polymers of "essentially infinite" MW, unless the entire mass of polymer produced were in one continuous phase, the actual molecular weight would be limited by the size of the individual droplets, beads, pellets, flakes, etc. No two of these would be likely to have exactly the same mass, and the distribution criterion would be met. For that matter, the molecular weight determination itself would produce a range of values because of the finite precision of the instrument.

ELEMENTAL EXCLUSIONS:

4. Regarding elemental limitations, why was fluorine not included in 723.250(d)(2)(B) but included in ii(C)?

Fluoride ion (F⁻) has a high acute toxicity, and would therefore be unacceptable as a counterion in a substance that is supposed to present no unreasonable risk to human health. Fluorine covalently bound to carbon is either unreactive and thus not available in the form of F⁻, or is part of a reactive functional group such as acyl fluoride (COF) and subject to the reactive functional group criteria.

5. Can you give an example of F⁻ (anion) that is not allowed?

Consider a cationic ion exchange resin that would otherwise have been eligible (because it meets the criterion of insolubility). If the counterion is fluoride (F⁻), it will be ineligible.

6. Ammonium is not listed as an acceptable monatomic counterion. Does this mean a polymer may be made under the exemption, but not its ammonium salt?

No; Ammonium may be used as a counterion. It is not monatomic, and is not excluded under section (d)(2)(ii).

7. Are only monatomic counterions allowed? What about CO₃²⁻, HCO₃⁻, NO₃⁻, etc.?

Monatomic counterions are allowed only if they are on a list of specifically allowed ones. All other monatomic counterions are excluded. The polymer exemption says nothing whatsoever about polyatomic counterions as such; they are permitted if they do not otherwise render the polymer ineligible. Carbonate (CO₃²⁻) is allowed, for example; perchlorate (ClO₄⁻) is not, because the chlorine is neither a monatomic ion nor is it covalently bound to carbon; trichloroacetate (CCl₃CO₂⁻) is allowed.

8. Are monomers that have CF₂ or CF₃ groups allowed?

Monomers that contain CF₂ or CF₃ groups are acceptable, provided that the groups are not part of a reactive functional group. -CF₂- is not generally a monomer unit because it is not "the reacted form of the monomer in the polymer"; however, -CF₂CF₂- groups derived from the polymerization of tetrafluoroethylene certainly could be monomer units.

EXCLUSION FOR DEGRADABLE POLYMERS:

9. What is the time frame for "polymers that do not degrade, decompose or depolymerize?" Does EPA want us to synthesize polymers that bioaccumulate in the environment? Does the term "degrade" apply to biodegradation or other degradation in waste treatment systems?

This restriction is essentially unchanged from the 1984 polymer exemption. While EPA recognizes in principle the beneficial effects of biodegradability, it commented in the discussion section of that rule that the Agency "...has little experience reviewing the mechanism by which breakdown may occur, the decomposition products that may result, and the potential uses of such polymers. ... Because of the complexity of review necessary for many of these polymers and the lack of EPA review experience, the Agency did not believe that an expedited review period was sufficient to adequately characterize risk."

The Agency acknowledged in that discussion that essentially all polymers degrade or decompose to a limited degree over time. It gave as examples the normal fate of polymers in landfills and the weathering of paint, and specifically stated that the exclusion was not intended to address such degradation. Substantial biodegradation in a waste treatment system would render a polymer ineligible for the exemption.

10. How does EPA define "degrade," "decompose," and "depolymerize?" If these are by-product minor reactions of a polymer, can the polymer still be eligible for the exemption, assuming other criteria are met?

The definitions are provided at §723.250(d)(3), and read: "For the purposes of this section, degradation, decomposition, or depolymerization mean those types of chemical change that convert a polymeric substance into simpler, smaller substances, through processes including but not limited to oxidation, hydrolysis, attack by solvents, heat, light, or microbial action." Minor byproduct degradative reactions will not exclude a polymer from the exemption; see the answer to the previous question, for example.

11. Starch is a polymer that readily degrades in the environment. If it were not listed on the TSCA Inventory, would starch be eligible for the exemption?

No; polymers that readily degrade are excluded from the exemption.

12. What does the Agency mean by "substantially" in the phrase "substantially degrade..."? Does this refer to any specific conditions (e.g., sunlight, water, low pressure) or under normal environmental conditions?

By "substantially," the Agency means considerably; meaningfully; to a significantly large extent. The restriction refers to polymers that undergo considerable degradation, under normally anticipated conditions of use or disposal, and in a reasonable length of time.

13. Will a polymer that is designed to be pyrolyzed or burned when it functions as intended be excluded from the exemption by the "degrade, decompose or depolymerize" conditions?

Yes, if that is the normal way it is used. A polymer propellant or explosive would be excluded. However, a plastic used for (say) garbage bags would not be excluded merely because it might under some circumstances be incinerated.

14. A manufacturer produces a polymer that is otherwise eligible for the exemption. It is readily biodegradable by the OECD test. There are two uses for the product. In one use, the manufacturer can reasonably anticipate that the polymer will eventually find itself in aqueous systems where it may degrade. In the second use, the polymer will be formulated into articles at a low percentage such that the articles themselves would not be anticipated to degrade once they are disposed of in a landfill. Provided that the manufacturer could control customer sales to assure that the polymer would only be used in the second use, could the polymer exemption apply?

Yes; provided that the use is restricted to conditions under which the polymer would not be expected to degrade, decompose or depolymerize, it would not be excluded from the exemption.

15. Will EPA specify testing conditions for evaluating "degradation"? Will manufacturers using the exemption have to test to prove their polymers don't degrade? Can we rely on intent to degrade?

This guidance document does not specify test conditions for degradability; there is no testing requirement to establish nondegradability; and, as the rule says in section (d)(3), polymers are excluded "...that could substantially decompose after manufacture and use, even though they are not actually intended to do so." In other words, it is what can actually be expected to happen to the substance, rather than just the intent of the manufacturer, that determines whether this criterion is met.

16. Are Diels-Alder polymers (for example, dicyclopentadiene polymers) considered degradable?

There are no specific constraints on structure or method of polymerization. If Diels-Alder polymers are "designed or reasonably anticipated to substantially degrade, decompose, or depolymerize," they would be excluded; if not, they would be eligible if the other exemption criteria are met.

EXCLUSION OF WATER-ABSORBING POLYMERS:

- 17. How are water-soluble, water-dispersible, and water-absorbing polymers distinguished with regard to the polymer exemption? Are they treated the same? Is dispersibility considered degradation?**

Water-soluble and water-dispersible (that is, self-dispersing or already dispersed) polymers are not considered to be water-absorbing substances. Only water-insoluble, non-dispersible water-absorbing polymers are excluded. The distinction is based on an assumed mechanism for lung damage by water-absorbing polymers, which involves a failure of the lungs to clear particles of these materials. Water-soluble or water-dispersible materials are expected to be cleared, and are thus not excluded. Dispersibility is not considered to be degradation.

A water-absorbing polymer that is manufactured or imported in water and is sold in water at concentrations allowing full water-absorption is not excluded from exemption provided that it meets all other criteria of the exemption and is not otherwise specifically excluded.

- 18. Why are high MW water-absorbing polymers excluded from the polymer exemption?**

EPA excluded this category of polymers from the exemption based on TSCA section 8(e) inhalation study, designated 8(e)-1795 and FYI-470, on a water-absorbing polyacrylate polymer with a MW in excess of 1 million daltons that indicated a potential cancer concern for this type of high MW water-absorbing polymer. The Agency concluded that exposure to respirable fractions of these polymers might present an unreasonable risk to human health. (For a discussion of this issue also see pages 16319-16320 in the rule which this document compliments).

- 19. If a polymer is partly ionized on use by a pH change which increases its water absorption to greater than 100 percent by weight, is the polymer no longer eligible for the exemption? What if the neutralizing agent is less than two weight percent of the polymer? Does the so-called "(h)(7)" pH neutralizer exclusion apply to polymers > 10,000 MW that absorb more than 100 percent of their weight of water upon neutralization? Does the "(h)(7)" exclusion take precedence over the polymer exemption, or vice versa, or what?**

If the polymer becomes water-absorbing upon use in neutral water, it is a water-absorbing polymer, whether or not ionization is involved.

If it is deliberately converted to a water-absorbing polymer by neutralization, that constitutes manufacture for commercial purposes as a chemical substance per se, rather than processing. The resulting substance would be a different polymer that would be considered water-absorbing and consequently not eligible for the exemption. (Even if the neutralizing agent used is less than or equal to two percent, a polymer must still meet the eligibility requirements in order to be exempt.) The unneutralized starting polymer could still be eligible for the exemption, if it met the other exemption criteria.

On the other hand, if the neutralization results in a substance excluded from reporting under 40 CFR §720.30(h)(7) (which basically covers processing rather than manufacture), that substance remains excluded from reporting even if it would have been ineligible under the polymer exemption. (See the Agency's published clarification on this issue available through the TSCA Assistance Information Service (202) 554-1404: the package from Joseph Carra, Deputy Director, Office of Pollution Prevention and Toxics, to the regulated community, dated June 29, 1994.) If an exempt polymer is converted into a water-absorbing substance as a result of a chemical process or reaction that

produces a substance excluded from reporting under (h)(7), the starting polymer remains exempt. Both the polymer exemption and 40 CFR §720.30(h)(7) apply, independently, to the respective substances.

20. I have an acidic resin that is eligible for a polymer exemption. Would the salt of this resin automatically be eligible for exemption?

A salt of an exempt polymer would not automatically be eligible for exemption. However, if the conversion of the resin to its salt introduces no properties (for example, water-absorption) or constituents (for example, certain elements in amounts greater than permitted) that would cause it to be excluded from the exemption, the resulting polymer salt should also be eligible for the exemption. The manufacturer must ensure that the polymer salt does in fact meet all requirements for exemption and that the reaction making the salt has not caused a change in the polymer which could exclude it from exemption. (Bear in mind that the conversion of a polymer to its salt does not always produce a reportable substance; see the answer to question 19.)

LIMITATION ON CATIONIC PROPERTIES:

21. If you have a very "non-basic" amine (such as dialkyl aniline) is it anticipated to become cationic in the environment? Suppose you can calculate from the pK_a of the amine and the concentration of amine groups in the polymer that the functional group equivalent weight of the protonated form of the amine will be >5000 in a natural aquatic environment. Could the polymer be eligible for the exemption?

If a manufacturer or importer can establish by pK_a data, or otherwise, that the amine groups in a polymer are "non-basic" and therefore would not become cationic in the environment, the polymer would not be excluded from exemption on the basis of potentially cationic character. However, amine groups are still considered reactive functional groups whether they are protonated or not. In other words, neither pK_a nor the "non-basic" character of amines affects the calculated reactive functional group equivalent weight. See the discussion under that section.

22. Does the phrase "used only in the solid phase" mean end use, as opposed to processing where the polymer may be melt extruded, injection molded, etc.?

"Used only in the solid phase" does refer to end use; a solid material melted during the course of processing does not have to be considered a liquid if it is solidified at the end of the processing step.

23. A polymer contains a potentially cationic group. The polymer is neither water soluble nor water dispersible but is manufactured by emulsion polymerization and therefore exists as particles dispersed in water. Is the polymer ineligible for the exemption?

Cationic polymers and potentially cationic polymers (see definitions in section 4.2.1 of this manual) are excluded from the exemption except for two types: 1) those that are solids, are neither water soluble nor dispersible in water, are only used in the solid phase and are not excluded by other factors; and 2) those that have low cationic density and are not excluded by other factors. If your polymer is neither water soluble nor water dispersible, manufacture by emulsion polymerization alone would not render it ineligible. See also the answer to question 17.

24. What exactly is meant by water-insoluble with respect to cationic polymers that qualify for exemption? Does the phrase "[T]he polymer is a solid material that is not soluble or dispersible in water" relate to a specific test? Is this a drop in water test or formulating test?

The phrase in section (d)(1)(i) does not relate to a specific test, and the Agency has not prescribed any specific test for water-solubility of

polymers. Whatever standard is used, however, should be applied to the commercial material as manufactured and sold. If an aqueous emulsion is the commercial form of the substance, the solubility criterion should be applied to that, rather than to a dried film of the final, end-use product. (An aqueous emulsion is a water-dispersed material, and a substance in that form would be considered to be soluble or dispersible; it therefore would not qualify.)

REACTIVE FUNCTIONAL GROUPS:

- 25. Please confirm that amine salts are permitted, as well as confirming that sulfonic and sulfuric acids (-SO₃H and -OSO₃H) and their salts are considered non-reactive.**

Amine counterions are permitted for anionic polymers. Sulfonate salts are not considered reactive. However, sulfonic and sulfuric acids are considered reactive (they were specifically designated as such in the 1984 polymer exemption rule, and the interpretation has not been changed in the new rule).

- 26. Regarding (e)(1) criteria, what are a few examples of "high concern" and "low concern" functional groups. Would acrylate, epoxide or isocyanate groups be considered "high" or "low" concern?**

Epoxides are listed in (e)(1)(ii)(B), the list of "moderate concern" groups for which concerns exist at a functional group equivalent weight of 1,000 or less. Acrylate and isocyanate are not listed either in (e)(1)(ii)(B) or in (e)(1)(ii)(A), the "low concern" group list; they are therefore considered "high concern" groups and fall under (e)(1)(ii)(C), for which the functional group equivalent weight concern level is 5,000 or less. Sections (e)(1)(ii)(A) and (B) contain lists of all the "low concern" and "moderate concern" groups, respectively. Any reactive group not on either list is considered to be "high concern."

- 27. The nitro group does not appear on the low- or moderate- concern list of reactive functional groups. Does this mean that nitro would fall into the high-concern category by default? This is counter-intuitive, because I wouldn't consider the nitro group to be very reactive and of much concern.**

Numerous groups were not listed because they were not considered to be reactive functional groups (for example, ester and ether groups). Nitro groups are also not considered to be reactive functional groups, unless they are specially activated (certain aromatic nitro groups are readily displaced by nucleophilic substitution reactions).

- 28. Is the amine group considered a high-concern reactive functional group? It is not listed specifically at either 40 CFR §723.250(e)(ii)(A) or (B), which would by default place it in category (C). However, because the criteria for a substance that "may become cationic in the environment" appears to address the concerns that EPA would have for amine groups in limiting the amount of amine in a polymer to one in 5,000 daltons, it does not seem that the amine group, in and of itself, should be regarded as a reactive functional group. Would the amine group be used in the calculation for FGEW_{combined}?**

The amine group is considered a high-concern reactive functional group and therefore should be used in the calculation. It is reactive in undergoing condensation reactions to form polyamides and polyimides and, unlike the aliphatic hydroxyl group, was not identified as a low-concern functional (category (A)) group. The Agency has concern for this group as a reactive functional group unrelated to considerations of its aquatic toxicity. For polymers that are not water-soluble or -dispersible and that will be used only in the solid phase, the limitation on cationic functional groups (such as quaternary ammonium) would not apply; but the limit on amine groups as reactive groups would still apply.

29. **Regarding FGEW of high concern groups vs. low concern groups, does one need to combine all high concern groups and separately combine all low concern groups - or add both together?**

If any "high concern" (that is, (e)(1)(ii)(C)) groups are present, one needs to calculate the combined functional group equivalent weight of any "moderate concern" (that is, (e)(1)(ii)(B)) and "high concern" groups together. To meet the criterion, the resulting FGEW must be no less than 5,000. "Low concern" (that is, (e)(1)(ii)(A)) groups are not included in the computation.

30. **If a polymer with a number-average molecular weight >10,000 meets the reactive functional group and oligomer content criteria of (e)(1), but not the more stringent oligomer content criterion of (e)(2), it seems to fall into a gap between (e)(1) and (e)(2). Is it therefore not eligible for the exemption? If is isn't, does the Agency plan to amend the (e)(1) criterion to omit the phrase "and less than 10,000 daltons"?**

The (e)(1) and (e)(2) exemptions are indeed mutually exclusive. Polymers with molecular weight of more than 10,000 are eligible only for the (e)(2) exemption, which has lower allowable concentrations of oligomer than does (e)(1). A polymer like the one described would not be eligible for either the (e)(1) or (e)(2) exemption. The Agency received no comment on this issue from the time the rule was proposed on February 8, 1993 until after the final rule became effective on May 30, 1995. A modification of the criteria seems reasonable, but additional rulemaking rather than a simple correction would be required. The issue is under discussion, and Agency resource constraints may rule out near-term action.

THE TWO PERCENT RULE (AND NON-INVENTORY REACTANTS):

31. **Please explain the changes in the "Two Percent Rule" for polymers.**

The "Two Percent Rule," which has been in effect since 1977, allows manufacturers and importers of polymers to add monomers or other reactants to an Inventory-listed polymer at levels of two percent or less (based on the dry weight of the manufactured polymer) without making a polymer with a different chemical identity than the Inventory-listed polymer. It also serves as a basis for determining the identity of a polymer. Before May 30, 1995, the effective date of the PMN Rule amendments, the monomer content of a polymer was always calculated based on the weight percentage of monomer or other reactant "charged" to the reaction vessel. The 1995 amendments allow persons greater flexibility in determining the percentage composition and whether monomers and other reactants are present at more than two percent. In addition to being able to use the "charged" method, the 1995 amendments allow persons to use an alternative method, i.e., to determine the amount of monomer or other reactant that is present "in chemically combined form" (incorporated) in a polymer and to report the minimum weight percent of that monomer or reactant that is needed in theory to account for the amount incorporated. A manufacturer is free to use either method to determine a two percent level; however the "incorporated" method, while providing more flexibility, also requires supporting analytical data or theoretical calculations.

This change in the "Two Percent Rule" applies to all polymers under TSCA, including Inventory listings, PMN submissions, and polymer exemptions.

32. **If I use the "chemically combined" method and claim that two percent or less of a reactant is incorporated in my polymer even though I charge a higher level to the reaction vessel, what records am I required to maintain to support this claim?**

Your records must contain analytical data or appropriate theoretical calculations, if such an analysis is not feasible, to demonstrate that the minimum weight of monomer/reactant required to account for the monomer/reactant fragments chemically incorporated is two percent or less. Your records should take into account potential batch-to-batch variation.

33. **It appears from the polymer exemption rule and the technical guidance manual that a person does not have the option of including a reactant/monomer at less than or equal to two percent in the polymer identity. Is this true?**

Yes, this statement is true. Polymers covered by a polymer exemption do not have a formal name. The "identity" is established by the percentages of monomers/reactants charged or incorporated in the polymer, as cited in the exemption-holder's records. If a polymer has less than or equal to two percent of a monomer/reactant, the identity does not contain that monomer/reactant. If an otherwise identical polymer is made, and the same monomer/reactant is a greater than two percent, the identity of the second polymer is different from the first. Two exemptions would have to be claimed to cover both polymers.

For polymers for which a PMN is submitted, the submitter does have the option of including a reactant/monomer at less than or equal to two percent in the polymer identity.

34. **Does a manufacturer need to test every batch of polymer to prove that less than two percent is incorporated, or would one documented test on a typical batch be sufficient?**

A company is not required to test every batch but is required to maintain in its records analytical data or theoretical calculations to demonstrate compliance with the "Two Percent Rule" when using the "incorporated" method. If the amount normally incorporated is expected to be close enough to two percent that occasional batches might exceed that level, either more frequent testing, or always considering the reactant to be part of the chemical identity, or manufacturing a separate exempt polymer with the reactant present at greater than two percent and included in the polymer identity, might be appropriate.

35. **I use a prepolymer that is on the Inventory to make my polymer. The prepolymer contains a non-Inventory monomer, and the final polymer contains greater than two percent of that monomer. Will my polymer be ineligible for the exemption?**

Not on the basis of the non-Inventory monomer; §(d)(4) bars the use of "monomers and/or other reactants... that are not already included on the TSCA Chemical Substance Inventory...", but the prepolymer is a reactant that is on the Inventory. The identity of the final polymer will probably include the non-Inventory monomer, though; see the answers to related questions in the section on Inventory Status of Reactants (questions 45-49).

36. **If an initiator is incorporated at no more than two percent, does it have to be on the TSCA Inventory?**

An initiator or other reactant present at no more than two percent does not have to be on the Inventory for a polymer to be eligible for the exemption. However, if the reactant is not on the Inventory, it cannot be used for commercial manufacture in the United States. Consequently, this provision will for all practical purposes be applicable only to imported polymers.

37. **Can I use less than or equal to two percent of any monomer that is on the Inventory?**

Yes, as long as that monomer doesn't introduce elements, groups or properties that would render the polymer ineligible at the concentration of monomer used. Note, though, that for the (e)(3) "polyester" exemption, all components of the polymer must be on the list of allowable reactants. In this case the use of non-listed monomers, even at two percent or less, would render the polymer ineligible for the (e)(3) exemption.

38. **I wish to import a substance containing greater than two percent of a reactant not on the public TSCA inventory, but which may be on the**

confidential inventory. On what do I file a Bona Fide, if all I plan to import is the final polymer, to know whether it now qualifies for the new polymer exemption criteria or if I need to file a PMN for the polymer?

There is really no way to find out whether a substance is on the Inventory unless you intend to import or manufacture that substance itself. You may not file a Notice of Bona Fide Intent to Manufacture ("Bona Fide") on the reactant unless you have a bona fide intent to manufacture or import it. (Your supplier, if in the U.S., could file a Bona Fide on the monomer, however.) Therefore, the only substance for which you can file a Bona Fide is the final polymer. If the polymer is on the Inventory, no PMN will be needed. If not, you will need to file a PMN for the polymer; unless you have a real intent to import or manufacture the monomer, you cannot file a PMN or an exemption for the monomer. If the monomer is on the Inventory, your polymer may be eligible for exemption. If it is not, completing the review process for the monomer and commencing its manufacture or import will allow it to be used in an otherwise exemptible polymer.

39. Can the polymer exemption be used for import of a polymer made with a non-TSCA listed chemical? If not, why?

The polymer cannot be imported under the polymer exemption if the non-TSCA reactant is used at greater than two percent. The reason is that the Agency cannot make the determination that no unreasonable risk will be incurred by a polymer that contains residual amounts of a monomer or other reactant that it has never reviewed. If the reactant is present at less than or equal to two percent, and if its presence does not otherwise render the polymer ineligible, the polymer may be imported (if eligible). A polymer may not be manufactured domestically if any reactant is not on the Inventory.

40. If a polymer is on the Inventory but contains a non-Inventory monomer, can you import it?

Yes. If the polymer is on the Inventory, it is an existing chemical, and no PMN or other notice or exemption is required. The exclusion of non-Inventory monomers and other reactants applies only to the polymer exemption. As in the answer to the previous question, you may not manufacture it domestically unless all the reactants are on the Inventory.

41. What if the non-Inventory-listed monomer is charged or incorporated at less than or equal to two percent?

A polymer containing a non-Inventory-listed monomer at less than or equal to two percent may be eligible for the exemption provided that the monomer does not "introduce into the polymer elements, properties, or functional groups that would render the polymer ineligible for the exemption". Language at §(g)(1) says that such reactants are not allowed "at any level"; but to the extent that below certain levels they do not render the polymer ineligible, they are not such reactants when used below those levels. Note again that a non-Inventory-listed monomer that is not on the list of permitted reactants for the (e)(3) exemption will render it ineligible for that exemption. There are in fact reactants on that list that are not on the Inventory. These are not subject to the two percent limitation, since they have already been reviewed by the Agency and are considered to be not of concern; see the answer to Question 50. However, if a monomer or other reactant is not on the Inventory or otherwise excluded from reporting or exempted from section 5 requirements, it cannot be used for domestic manufacture, regardless of its concentration in the product polymer.

42. Can polymers that utilize less than or equal to two percent of non-Inventory listed monomers be eligible for the exemption?

Such polymers would be eligible for exemption as long as they meet all the other exemption criteria. However, a monomer used at any concentration

must be on the Inventory or exempt before it can be used in the domestic manufacture of the polymer.

- 43. If a polymer contains any amount of a component that is not on the TSCA inventory, it cannot be manufactured domestically under the polymer exemption. Does that mean that a PMN for the polymer is necessary, or does it mean the reactant must be put on the Inventory first before the polymer exemption can be used?**

To use a substance domestically for any reason, it must be on the Inventory, excluded from reporting, or exempted under an applicable section 5 exemption (for example, low volume exemption, low release and exposure exemption, pre-1995 polymer exemption, current polymer exemption). Therefore, a PMN (or applicable section 5 exemption) is required for the new reactant, and the reactant must be on the Inventory or exempt before it can be used in the domestic manufacture of the polymer. Once the reactant is on the Inventory, a polymer containing it would not be automatically excluded from the exemption, as long as it was otherwise eligible.

- 44. If you have a TSCA-listed brominated flame retardant mixed at greater than two percent in a polymer base, is the polymer subject to PMN requirements or is it exempt?**

The material is considered to be a mixture of polymer and the flame retardant. Mixtures are not subject to reporting under TSCA, provided that there is no intended reaction between the components of the mixture. The components of the mixture are separately subject to reporting if they are not on the Inventory. If they are both on the Inventory, no reporting is required. If the polymer is eligible for the exemption, the presence of the other component will not render it ineligible.

- 45. Are all of the exclusions under 40 CFR §720.30 ("Chemicals not subject to notification requirements") applicable to the polymer exemption?**

Yes; however, a manufacturer must comply with the conditions of the exclusions even though the substances are being used in connection with the polymer exemption. For example, a substance subject to the low-volume exemption could be used as a monomer for an eligible polymer, but only if the supplier is a holder of the exemption and if the appropriate production ceiling is adhered to.

INVENTORY STATUS OF REACTANTS; CHEMICAL IDENTITY OF POLYMERS:

- 46. How do I find out whether:**
(a) my polymer is on the confidential TSCA Inventory?
(b) a reactant in my polymer is on the confidential Inventory?

You can determine the Inventory status of your polymer by filing a Notice of Bona Fide Intent to Manufacture (or a PMN). You may not file a Bona Fide on the reactant unless you have a bona fide intent to manufacture or import it. It is the responsibility of the manufacturer or importer (your supplier, in this case) of the reactant to determine the Inventory status of the reactant.

- 47. When a prepolymer is one of the precursors of a polymer, what should be considered to be the constituents of the final polymer: the ultimate reactants from which the prepolymer was manufactured, the prepolymer itself, or what?**

The choice should follow Chemical Abstracts (CA) nomenclature rules and conventions for its Ninth Collective Index (9CI). In general, polymers are named on the basis of their ultimate monomers. Thus the name of a prepolymer derived from dimethyl terephthalate and 1,4-butanediol would be based on those reactants. However, there are some exceptions to this generalization. For example, although polyethylene glycol may be thought of as a homopolymer of ethylene oxide, it is not named as a homopolymer under CA naming practices,

but rather according to the structural repeating unit (SRU) and end groups present: α -Hydro- ω -hydroxy-poly(oxy-1,2-ethanediyl). Similarly, polydimethylsiloxane is named on the basis of its SRU: di-Me Siloxanes and Silicones (and is considered to be end-capped with trimethylsilyl groups). If a prepolymer is named so as to represent a certain structural feature or definite repeating unit, its name cannot be decomposed into ultimate monomers for the purpose of naming the final polymer. The Agency's conventions for representation of polymeric substances are discussed in greater detail in a 1995 paper, "Toxic Substances Control Act Inventory Representation for Polymeric Substances," available from the TSCA Hotline: phone (202) 554-1404; fax (202) 554-5603.

48. Does the "Two Percent Rule" apply to the actual reactants used, or to the ultimate or putative reactants?

Consistent with the answer above, the ultimate reactants should be the basis of the chemical identity of the polymer. Thus, if a new polymer is made from the polymer in the answer above, plus additional dimethyl terephthalate and ethylene glycol, the final polymer name would be based on three constituents, and the total amount of dimethyl terephthalate would be the sum of the separate contributions. Ultimate reactants that contribute no more than two percent by weight to the final polymer may be omitted from the identity. If a homopolymer is used as a prepolymer constituent, the identity of the derived polymer should be based on the ultimate monomer, except where CA practice differs due to the applicability of SRU nomenclature (see the paper referenced in the answer to the previous question). Although calculation of the percentage composition of a polymer may be based on analysis (that is, "incorporated"), the identity should be based on the ultimate precursors.

49. In light of the modified "Two Percent Rule," which now allows reporting of polymers as incorporated as well as charged, can all polymer listings on the Inventory now be read either as incorporated or as charged?

Yes; polymers on the Inventory can be interpreted either as incorporated or as charged. Remember that "incorporated" means the minimum amount that theory requires to be charged in order to account for the amount monomer or reactant molecules or fragments found in the polymer itself.

50. If I import a polymer that is described as a sodium salt and I can determine analytically that sodium is present at two percent or less, can I assume that sodium hydroxide was the neutralizing agent used to produce that material, and should I use the sodium hydroxide molecular weight in determining the percent incorporated (and hence the chemical identity)?

Yes; in the absence of information about the source of the sodium ion, sodium hydroxide should be used as the default source and the calculations should be based on the molecular weight of sodium hydroxide. The hydroxides of magnesium, aluminum, potassium and calcium should also be used as the default sources of the respective ions.

POLYESTER CRITERION:

51. Some of the reactants on the polyester list are not on the TSCA Inventory. Am I allowed to use these to manufacture a polyester under the polymer exemption?

Yes, for imported polymers. Under the 1984 exemption those reactants were placed on the polyester ingredients list, even though they were not on the Inventory, because there was no exclusion for non-Inventory reactants. The Agency is continuing to allow these specific reactants, because the Agency has already made the determination that no unreasonable risk will be incurred by a polymer that contains residual amounts of these reactants.

For domestic manufacture, you may use only substances that are on the Inventory or are otherwise exempt or excluded from reporting.

52. **If a monomer in my polyester is used at less than or equal to two percent and is not on the (e)(3) list, is the polymer eligible for the exemption if it meets all the other criteria and is not otherwise excluded from the (e)(3) exemption?**

No, the polyester would not be eligible for the exemption. Only monomers and reactants on the (e)(3) list may be used for this category of polymer regardless of the percentage charged or incorporated.

53. **Is there to be a mechanism to add new reactants to the polyester reactants list? If so, what is expected to be required?**

The list of permissible ingredients in the present exemption has already been enlarged since the 1984 version. To quote from the Agency's response to a comment addressing this specific issue in the preamble to the final rule, "The Agency believes that it would be appropriate in the future to propose amendments to this section to allow expansion of the list of eligible precursors, when additional candidates have been identified. To support requests for additional reactants, petitioners should provide health and environmental effects information on the candidate reactants, which must be already on the Inventory." No specific mechanism has yet been put in place. The Agency would prefer not to deal with such reactants piecemeal, but rather as part of a systematic process, perhaps initiated by trade organizations or consortia of interested companies.

OTHER ISSUES:

54. **If a polymer contains a gel fraction (presumably high MW>10,000) of 10 to 20 percent and the MW of the soluble fraction is <10,000, is it no longer exempt? Or is the gel fraction an impurity? Or by-product?**

Since the two polymeric fractions have the same chemical identity and are not separately prepared, they would usually be considered as a single substance, for which one (not two) number-average molecular weight would be measured. However, impurities are not considered part of a polymer composition; if the 10-20 percent gel portion is undesirable, it may be considered an impurity. In that case, the appropriate number-average molecular weight would be for the portion below 10,000, and the polymer would have to meet the (e)(1) criteria. Whether the gel portion is considered an impurity does not depend upon whether it is a minor component; it depends upon whether it is not intended to be present.

55. **Are inventory-listed monomers which have allowed groups, and a 5(e) order attached, eligible for the new polymer exemption?**

Yes, as long as the use of the monomer is in accordance with the conditions of the 5(e) order.

56. **There is no guidance on measurement of oligomer content. Is accumulated weight fraction on a GPC trace an adequate determination? In the absence of GPC, how can this be done?**

Cumulative weight fraction is a commonly accepted method. The Agency has not prescribed any analytical methodology; others may be acceptable, depending on circumstances.

57. **Do polymers made by "reactive processing" of two or more other polymers (both on TSCA) fall under the polymer exemption?**

If not otherwise excluded, yes, as long as they meet the necessary criteria. There is no exclusion for polymers made from other polymers, nor is there any restriction on method of preparation.

58. **What are the analytical requirements with respect to insoluble polymers? Can inference from melt flow data and comparison to other polymers be**

adequate? Can I use Monte Carlo simulation methods (such as Oligo 5) to estimate the MW of an insoluble polymer theoretically?

The Agency does not require any specific analytical methodology. Inference from physical behavior, from comparison to close analogues, and from theoretical calculation is acceptable where appropriate or where other methods are inapplicable. Monte Carlo methods, while widely used, have not been subjected to much experimental verification; if your polymer is expected to have values of MW or oligomer content near the allowable thresholds, you should probably not rely too strongly on such methods. For a discussion of analytical methods in general, see the relevant section of this guidance manual.

59. For persons who choose to use the "chemically combined" method for determining the amount incorporated in a manufactured polymer, does EPA prescribe a specific analytical method for this determination?

No. The rule does not specify any particular method. Guidance on this issue is found in this guidance manual.

60. If you make a new polymer in the laboratory which meets the exemption rule, do you need to send a research and development letter to the customer?

Substances considered to be research and development (R&D) chemicals are subject to the Research and Development Exemption, and must follow the conditions of that exemption. Polymers should be handled according to the R&D requirements until they reach the stage of being commercial products eligible for the polymer exemption. When the commercial activity is no longer R&D, provisions of that exemption no longer apply.

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