TOXIC SUBSTANCES CONTROL ACT
INVENTORY REPRESENTATION FOR

COMBINATIONS OF TWO OR MORE SUBSTANCES: COMPLEX REACTION PRODUCTS

I. Introduction

This paper explains the policies that are applied to listings of reaction product combinations of two or more substances for the Chemical Substance Inventory that is maintained by the U.S. Environmental Protection Agency (EPA) under the Toxic Substances Control Act (TSCA). For purposes of this paper, only combinations that result from chemical reactions are considered. Mixtures that do not result from a chemical reaction (i.e., formulated mixtures) are covered in a separate guidance document. The Agency's goal in developing this paper is to make it easier for the users of the Inventory to interpret listings for reaction products and to understand how new complex substances would be identified for Inventory inclusion.

Fundamental to the Inventory as a whole is the principle that entries on the Inventory are identified as precisely as possible for the commercial chemical substance, as reported by the submitter. Substances that are chemically indistinguishable, or even identical, may be listed differently on the Inventory, depending on the degree of knowledge that the submitters possess and report about such substances, as well as how submitters intend to represent the chemical identities to the Agency and to customers. Although these chemically indistinguishable substances are named differently on the Inventory, this is not a "nomenclature" issue, but an issue of substance representation. Submitters should be aware that their choice for substance representation plays an important role in the Agency's determination of how the substance will be listed on the Inventory.

Each combination of substances resulting from a reaction is considered by the Agency to be either (1) a mixture, composed of
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two or more well-defined chemical substances to be named and listed separately, or (2) a reaction product, to be listed as a single chemical substance, using one name that collectively describes the products, or, failing that, the reactants used to make the products. The submitter's commercial intent (or author emphasis) plays an important role in the Agency's determination of whether a particular reaction product combination is treated as a mixture or as a reaction product. The choice between these two possibilities becomes especially difficult when a seemingly reasonable representation of the products of a reaction may be made using either option. This paper explains the policies that are used to determine whether a complex reaction product that contains multiple components should be represented as one complex

reaction product or as its individual components for purposes of the TSCA Inventory.

It is often difficult to determine if a complex reaction product combination should be reported as a reaction product (a single Inventory listing comprising the combination as a whole) or as a mixture. The choice between the two depends upon both the chemistry of the product and the commercial usefulness of the substance. The Agency allows submitters some flexibility in describing their substances to EPA; however, once the submitter's substance is listed on the Inventory, the future flexibility is gone with respect to that particular substance and a manufacturer or importer (and all subsequent manufacturers or importers of essentially the same product) either must identify his or her product with a name that exactly matches an Inventory listing or must submit a PMN for their "new" substance.

II. Inventory Policies with Illustrative Examples

A. General Discussion

1. Chemical Classes and Applicable Nomenclature Rules

Each component of a product combination that is listed on the Inventory has been named by the Agency using Chemical Abstracts (CA) nomenclature. A chemical substance that can be represented by a definite chemical structural diagram and molecular formula is a Class 1 substance. Examples of Class 1 substances are acetone, iron, benzene and sodium chloride.

Identities of product substances which are combinations of different known or unknown species or whose composition cannot be represented by a definite chemical structure diagram are Class 2 substances. Among the Class 2 substances are those that are of Unknown or Variable compositions, Complex reaction products or Biological materials (UVCBs). Examples of Class 2 substances are cresol, crude oil, superphosphate (fertilizer), tall oil and coconut oil fatty acids.

2. Inventory Names for UVCB Chemical Substances

For a complex reaction product that is not intended to be polymeric and for which there is no definite or known molecular formula or chemical structure information, a single substance name is developed. This one name encompasses the various molecular entities that are likely to be present in the complex reaction product.

For these substances, definitions are often developed to supplement the chemical names if the name itself does not adequately define the characteristics and limitations of the substance category. The definition often describes the scope of composition by indicating such information as the typical or allowed carbon number ranges or physical property ranges, the types of atoms or substances that may be included, and the allowed raw material sources or processes of manufacture. For all substances that have a supplemental definition, that definition is considered to be part of that name for TSCA purposes. Regardless of whether a supplemental definition is developed for a complex substance, it is Agency policy to incorporate reported information about specific sources of materials or manufacturing processes into the actual chemical

names for complex substances.

When the composition of the product combination is very difficult to define except in very broad terms, or if different types or classes of (non-polymeric) reactions occur simultaneously to yield a very complex set of products, a "reaction products" type of name is used. The chemical names of all reactants are identified using the phrase "reaction products with." An example is Carbonic acid disodium salt, reaction products with aniline, 4-nitrobenzenamine, p-phenylenediamine, sulfur and p-toluidine, CASRN 138063-69-1*.

The commercial intent behind this type of substance is important as well. For substances named as "reaction products with," all of the components that might be present in the reaction product would be present intentionally and have commercial value. If only some of the components within the product were present intentionally and of commercial value, the rest of the components would be considered as impurities and the name assigned would include only the commercially-valuable components. If only one chemical component were of commercial value, the reaction product would be named using that component.

A substance named as "reaction products with" does not allow manufacturers to change the reactants used, even if a chemically identical product could be formed with a different set of reactants; any substitution of reactants would create a different chemical substance for TSCA Inventory purposes. Substance names that include "reaction products with" indicate very little about the chemical nature of the products; thus, the Agency avoids using these names unless there is no alternative.

3. Mixtures that result from chemical reactions

Before compiling the Initial Inventory, EPA decided that naming substances consistently and as specifically as possible should be a key element of the Inventory to maximize its effectiveness for implementing TSCA. Maximum specificity facilitates the accurate determination of the Inventory status of a potentially new substance. For this reason, the Agency believes that the identity and range of composition (in weight percent) of each chemical substance in a product combination should be reported as completely and specifically as it is known to the submitter, or insofar as this information is reasonably ascertainable. Whether a product combination can be treated as a mixture and each separate component listed on the Inventory depends on the nature of the reported chemical identity information and the intent of the submitter.

4. Mixtures of salts

When compiling the Initial Inventory, EPA recognized that certain industries could incur excessive reporting burdens involving their chemical products. For example, some reporting relief was granted to soap and detergent manufacturers for "deliberately manufactured mixtures" of salts of monovalent anions. Consultations and agreements between the Agency, the Soap and Detergent Association (SDA) and Chemical Abstracts Service (CAS) resulted in the following Agency Inventory convention, which appears on page 7 of Addendum III to the TSCA Candidate List of Chemical Substances:

"Mixed salts of monovalent anions are considered mixtures of

the individual salts, each of which should be reported separately."

The intent of this convention is to allow a salt combination containing one or more new substances to be named and listed as the individual salts, instead of having the whole combination considered as one new substance by the Agency. As a result, salts involving only monovalent anions are in most cases considered to be mixtures of the monovalent salts; these individual salts are then listed as single substances on the Inventory. (Refer to Section B below for exceptions.)

The unstated but implicit corollary to this convention is that mixed salts of ions that are other than monovalent are not automatically to be considered as mixtures of individual salts. For example, if a diacid reacts with two or more bases, crossproducts would likely be formed and there would likely be uncertainty about the composition of the product. Any uncertainty would result in one name for the composition as a whole. However, a given crossproduct combination could sometimes be treated as a mixture, if it meets the criteria listed in Section B, below.

This Inventory practice was established to ease the reporting burden of manufacturers who find it more economical and simpler in terms of processing to synthesize a blend of salts simultaneously in the same reaction vessel, instead of mixing the separately manufactured substances. It is illustrative of the Agency convention of providing specific Inventory entries for each component of a reaction product combination for which the submitter has identified all of the components.

A similar approach was adopted for certain combinations of organic compounds and other types of mixed salts, allowing them to be considered as mixtures and their components represented as individual substances on the Inventory. This convention covers relatively complex combinations as well as simpler reactions that produce "intentional" product mixtures of organic compounds or salts, as long as all of the individual product components were fully identified substances. The term "intentional" refers in this context to the deliberate, simultaneous synthesis of similar products in one reaction vessel, utilizing different (usually competing) reaction pathways. The Agency considered these decisions to be consistent with the Congressional intent for EPA to implement TSCA in a reasonable and prudent manner with consideration of the economic and social as well as environmental impacts of the Act.

5. Author Emphasis; Submitter Representation

Substances that are chemically indistinguishable, or even identical, may be listed differently on the Inventory, depending on the degree of knowledge that the submitters possess and report about such substances, as well as how submitters intend to represent the chemical identities to the Agency and to customers. The Agency may name two chemically indistinguishable combinations differently for the Inventory because, what one submitter may consider to be a minor component intentionally present, another may consider to be (1) an impurity or (2) a byproduct having no commercial purpose that is inadvertently present.

Impurities or byproducts having no commercial purpose are not included as part of the chemical identity of a complex

reaction product. Rare exceptions may occur, however, for poorly-described substances such as those named as "reaction products with." In these exceptional cases, it may not be possible for the submitter to distinguish the intended products from impurities and byproducts.

The intent of the submitter, as stated or implied in the reported information, is also important in helping EPA to determine if a product combination should be considered a mixture under TSCA or given one name as a complex reaction product. The following kinds of information are always considered by the Agency for the purpose of establishing chemical identity for a complex reaction product:

(1) the chemical reactants or feedstocks used by the submitter;
(2) the nature of the manufacturing process;
(3) the submitter's ability to identify the individual components in the product;
(4) whether the components will be separated and marketed individually, now or in the future;
(5) whether certain product components may be considered as impurities or as byproducts having no commercial purpose; and
(6) how the submitter represents (or intends to represent) the chemical composition of his or her product to customers.

These types of submitted information often contribute to the Agency's application of conventions for deciding whether a whole product combination should be represented as one substance and given one name, or whether the product components should be named separately as a mixture.

B. Statement of Conventions for Inventory Representation

1. Product Combinations that are generally mixtures

a. A combination of products resulting from a chemical reaction is considered a mixture provided that all of the component product substances are unambiguously identified and are represented as forming each time the reaction is run.

In this case, each component of the mixture requires a separate listing on the TSCA Inventory. This convention applies to a complex reaction product that is well-characterized, as well as to a simpler reaction product combination that is manufactured intentionally for the purpose of convenience or economy (instead of blending two or more products from reactions carried out separately).

Economic factors, such as the cost of the commercially-available ingredients, are not considered to be a factor in determining whether the combination could have been prepared for commercial purposes by mixing. If the performance characteristics and chemical composition of the combination prepared by mixing would be essentially identical to that of the combination prepared by chemical reaction (disregarding any impurities), the combination prepared by mixing could be expected to serve the same "commercial purpose" and the combination would be considered to be a mixture.

b. For reactions of acids and bases that can yield combinations of salts, the simple (1:1) ion pairs that can result from the use of only monovalent reactants are usually considered to be a mixture.

2. Product Combinations that are generally chemical substances

a. If there is some uncertainty or ambiguity in the identity of one or more substances in a product combination (as in most complex reaction products), or if it is not certain whether each substance is formed every time the reaction is run, then the combination is given one name that collectively describes either the products or the reactants of the reaction.

Such a single name is preferably based on the products of the reaction. However, if the products of such a combination consist of different chemical classes of substances, or are unknown or too complex to reasonably constitute a product-based name, a "reaction products" name is used, which is based on the reactants. It is Agency practice that names including the phrase "reaction products with" include all reactants, regardless of the amounts used. Unlike the Inventory convention for polymers, there is no "two percent rule;" there is no flexibility for this type of complex substance listing to cover the use of small amounts of other reactants not listed in the name of an otherwise matching Inventory substance.

b. If two or more bifunctional or polyfunctional substances are reacted with each other, the resulting product combination (e.g., polymer, reaction products) as a whole is represented by one name.

A reaction product representation of a polymeric or non-polymeric substance based on the names of the reactants or monomers is usually used. Details on polymer nomenclature, including SRU representation, are found in another paper in this series.

C. Application of Conventions: Examples

1. Mixtures synthesized from monofunctional precursors

Example 1. Consider a reaction in which three monofunctional substances react to give just two products. In generic terms, monofunctional substances A, B and C react to yield products AB plus AC, with no reaction between B and C:

A + B + C ----------> AB + AC

A more specific example of such a reaction involves a monofunctional carboxylic acid (RCOOH) reacting with two different alkyl alcohols (R'OH and R"OH), where R, R' and R" are different alkyl groups:

2 RCOOH + R'OH + R"OH -------> RCOOR' + RCOOR" + 2H2O

Because there is only one functional group on each molecule,

the only two possible products are the esters RCOOR' and RCOOR". There is no chemical exchange occurring between the two alcohols themselves, and no reaction occurs between the two products. Since the product identities are known without ambiguity, the two esters constitute a mixture according to Inventory convention, and are named separately.

Using this example of ester formation, a product combination from the reaction of propanoic acid with ethanol and 1-hexanol (all monofunctional reactants) would be represented as a mixture of two product components listed separately on the Inventory: (1) Propanoic acid, ethyl ester, CASRN 105-37-3; and (2) Propanoic acid, hexyl ester, CASRN 2445-76-3.

Having a product named as individual components may have a useful benefit for the manufacturer: since the components are listed separately on the Inventory, the manufacturer has the flexibility to produce any one component separately without creating a new chemical substance that might require PMN review.

Example 2. To illustrate the application of Inventory conventions to salt formation, consider the hypothetical case of a manufacturer intending to make a new product consisting of a blend of the sodium, potassium and lithium salts of a certain carboxylic acid. In this example of an intentional reaction mixture, the salts would be produced together, for convenience, in the same batch by simultaneously reacting one monovalent acid (RCOOH) with three monovalent bases, sodium hydroxide (NaOH), potassium hydroxide (KOH) and lithium hydroxide (LiOH):

$$3\ RCOOH + NaOH + KOH + LiOH \longrightarrow RCOO\text{-}Na^+ + RCOO\text{-}K^+ + RCOO\text{-}Li^+ + 3\ H_2O$$

Even if the manufacturer does not intend to market the salts separately, this type of product combination would be called a mixture. The individual salts (RCOO-Na+, RCOO-K+ and RCOO-Li+ in the example reaction) would be named and listed as separate substances on the Inventory. These three salts could be present in any ratio.

This rule would also apply in the case of salts formed in an opposite manner by reacting several different monovalent acids with one monovalent base, in any ratio. Furthermore, reacting m different monobasic acids with n different monoacidic bases would, in principle, yield a product combination considered by EPA to be a mixture of discrete salts of all the (m times n) possible ion pairings. The policy allows for the naming and listing of all the possible salt products from such a reaction that are new substances.

Example 3. If a UVCB substance is known to be a monofunctional reactant in a salt-forming reaction, it will form a mixture of salts when reacted with potassium hydroxide and sodium hydroxide; each salt would be listed separately on the Inventory. On the other hand, if the UVCB substance is known to be multifunctional or if the number of functional groups is unknown, reaction with potassium hydroxide and sodium hydroxide is considered to yield a single substance for TSCA purposes composed of potassium and sodium mixed salts.

2. Intentional Mixtures involving at least one reactant that is not monofunctional

Example 4. Consider the reaction of an excess of a bifunctional precursor, hexanedioic acid, with one monofunctional alcohol, ethanol:

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    HOOC-(CH2)4-COOH        +          CH3CH2OH  ----->
(excess hexanedioic acid)              (ethanol)


CH3CH2OOC-(CH2)4-COOH      +      CH3-CH2OOC-(CH2)4-COOCH2CH3
 (monoester product)                    (diester product)
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Assume that although there are not enough reaction equivalents of ethanol to react with all of the carboxylic acid groups of hexanedioic acid, the ratio of equivalents of the starting materials is controlled so that two products form in this reaction instead of just one. If this product combination has been characterized to establish conclusively the presence and identities of both products, and there is enough quantitative evidence to suggest that useful amounts of both products are always formed, then such a reaction product would be considered a mixture. The two products would be represented separately as: (1) hexanedioic acid, monoethyl ester (CASRN 626-86-8) and (2) hexanedioic acid, diethyl ester (CASRN 141-28-6).

If the submitter had not reported a knowledge of the relative ratio of the reactants, or whether useful amounts of both products will always be formed, or whether the second esterification step proceeds with the same facility as the first, the product would be represented by the Agency as a single, Class 2 substance: Hexanedioic acid, ethyl esters.

3. Complex Reaction Products

Example 5: In generic terms, suppose that substance A is a bifunctional reactant, and substances B and C are monofunctional co-reactants that do not react together by themselves (but each reacts with A). There would be five possible products if the two functional groups of A are the same and are in equivalent structural positions in the molecule (i.e., are symmetrical):

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A  +  B  +  C  ----->  B-A-B  +  B-A-C  +  C-A-C  +  A-B  +  A-C
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If the functional groups of A are not identical or equivalent, eight structurally different products could form:

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A  +  B  +  C  ----->  B-A-B  +  B-A-C  +  C-A-B  +  C-A-C
                       +  A-B  +  B-A  +  A-C  +  C-A
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(A-B, A-C and B-A-C are structurally different from B-A, C-A and C-A-B, respectively)

On the other hand, the stoichiometry of the reaction could simplify the combination by eliminating certain products. For example, a large excess of B and C relative to A would be expected to eliminate the formation of the binary products (A-B, B-A, A-C and C-A) if both functional groups

of A are of similar reactivity. Such a stoichiometric imbalance in the reactant equivalents could reduce the number of products to four, or even three. If all the products formed in a defined reaction are known and consistently present, then each would have a separate Inventory listing. Otherwise, one name would be used for the whole reaction product.

Example 6. Consider the reaction of hexanedioic acid (a bifunctional substance having two identical reactive groups at equivalent positions in the molecule) with an excess of two aliphatic, monofunctional alcohols, 1-octanol and 1-decanol. This reaction was reported as yielding three possible diester products in an unknown ratio; because the ratio of the two alcohols varied widely, it was uncertain whether all three products are always formed.

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HOOC-(CH2)4-COOH + R'OH + R"OH  ----->  R'OOC-(CH2)4-COOR'
                                        +  R'OOC-(CH2)4-COOR"
                                        +  R"OOC-(CH2)4-COOR"
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where R' = octyl and R" = decyl

Although the two alcohols do not react with each other, they can both react with the same diacid molecule. One of the possible products, the mixed diester R'OOC-(CH2)4-COOR", would directly result from this chemical exchange between all three of the reactants and contain parts of all three starting materials.

Due to the uncertainty of the specific composition of this reaction product (unknown ratio of reactants and uncertain products formed), it was represented as one collective substance, and was listed under one UVCB name: Hexanedioic acid, mixed decyl and octyl esters (CASRN 68307-93-7*).

Example 7. Consider a similar reaction: hexanedioic acid is reacted with a two-mole excess of both 1-octanol and 1-decanol, with the two alcohols used in roughly equal amounts. The reaction diagram from the previous example would still apply.

Suppose that this product combination is reported to be composed of just the three diesters shown above, which are unambiguously identified and known to form every time the reaction is carried out in this manner. The product combination would then be considered a mixture of three separate substances:

(1) Hexanedioic acid, dioctyl ester (CASRN 123-79-5)
(2) Hexanedioic acid, decyl octyl ester (CASRN 110-29-2), and
(3) Hexanedioic acid, didecyl ester (CASRN 105-97-5).

The different ways in which the product combinations in the last two examples are represented for Inventory purposes are a reflection of the degree of certainty with which the submitter specifies the ratio of the alcohols used in excess, and, therefore, his relative certainty about the specific product composition.

Example 8. Another example of a complex reaction product involves the reaction of decanoic acid, octanoic acid and valeric acid (three monofunctional carboxylic acids) with

dipentaerythritol (a polyfunctional alcohol). The stoichiometry is not specified. In theory it is possible to identify the many products of this reaction and give each product a specific name for Inventory listing purposes. However, the submitter did not unambiguously identify all of the component product substances and did not represent all of them as forming each time the reaction is run. The Agency elected to use one UVCB name to represent the whole product combination: Decanoic acid, mixed esters with dipentaerythritol, octanoic acid and valeric acid (CASRN 68441-66-7*).

The only specific product information given by this Class 2 name is that only ester moieties (involving decyl, octyl or pentyl groups) are formed by the reaction. However, the term "mixed esters with" provides a more precise and useful representation than would exist if this term were replaced by "reaction products with."

The Agency does not use an explicit criterion to determine when it is not practical to identify and enumerate the components of a complex reaction product combination. However, the author emphasis conveyed by the submitter and the commercial intent that can be inferred from the reported information are carefully considered by the Agency in determining which type of reaction product representation is appropriate.

Example 9. The reaction of phosphoric acid (a tribasic acid) with one monovalent base, sodium hydroxide, and one divalent base, magnesium hydroxide, yields an uncertain and complex set of reaction products. The possible salts comprising this product combination are represented as one substance: phosphoric acid, magnesium sodium salt (CASRN 25640-28-2*). As Class 2, this substance is unspecified with respect to the ratios of metal ions to the conjugate bases of phosphoric acid.

Example 10. Some complex reaction products have definitions that further describe the substances. One such substance is: Distillates (petroleum), steam-cracked. CASRN 64742-91-2*

The definition that goes with this name is: A complex combination of hydrocarbons obtained by distillation of the products from a steam cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly in the range of C7 through C16 and boiling in the range of approximately 90 degrees C to 290 degrees C (194 degrees to 554 degrees F).

This definition is legally part of the substance name for TSCA purposes. A second substance being compared to this one is not considered to be identical unless the characteristics of the second substance agree with those in the definition of the Inventory substance. Persons using the TSCA Inventory listings, especially the various on-line versions, need to be certain that they obtain any definitions that may pertain to substances of interest before they make Inventory determinations. The definitions are usually found in fields separate from the main names, and so may be overlooked.

4. Names Containing "Reaction Products with"

Some complex manufactured products including non-polymeric polyamide resins constitute a category of substances that is represented by UVCB (Class 2) names containing the phrase "reaction products with." So little is known about the chemical structures of these products that the names contain the reactants rather than a description of the products as with all other names.

Example 11. Diethylene triamine reacts with dimer C18-unsaturated fatty acids to yield the type of short chain polyamide resin typically used as an epoxy curing agent. In addition to the basic amidoamine functionality present in the resin, such other products as amine salts and those containing imidazole rings may form.

The formation of these extra types of products, which is often intentional, causes this resin to be unsuitable for definite structural diagramming and molecular formula representations. In addition, it is difficult or impossible to assign a product-based name that accurately describes the chemical composition of the reaction product. Consequently, this product combination is represented as a Class 2 substance and assigned a "UVCB reaction product" type of name based on the reactants: Fatty acids, C18-unsatd., dimers, reaction products with diethylenetriamine (CASRN 68410-22-0*). This nomenclature is appropriate for compositions that are primarily adducts.

If an amine reacts with an acid, forming solely amides, the product is named as an amide. If the product is an amine salt and the heading parent is an acid, the name would usually be of the format: "acid, compd. with amine." An example of an exception is with acetates, where, in generic terms, the name format is: "Amine, acetate." If the product contains both amine salts and amides, it would be named as a reaction product.

5. Impact of Submitter Representation

There may be regulatory consequences of a submitter's choice for substance representation, both for the submitter directly and for any subsequent manufacturers or downstream users of the submitter's product.

Example 12. If a person first chose to represent a product combination according to the specific name of one of the components (because other components were considered to be impurities of no commercial value) and later decided to separate and market a second product component from that reaction, a PMN would be required if the second component itself was not already listed on the Inventory.

Example 13. If a person initially used one Inventory listing to represent a complex product combination as a whole because it had an indefinite composition, but later wanted to market one or all of the components separately, PMN reporting would be required to cover the desired individual product component(s) not already on the Inventory.

A submitter should be aware that if customers are using a product in subsequent reactions to manufacture other products, any change in the submitter's representation of the chemical

identity of his/her product would likely jeopardize the TSCA compliance of the customers' down-stream products.