

**HIGH PRODUCTION VOLUME (HPV)
CHEMICAL CHALLENGE PROGRAM**

TEST PLAN

for

**ROSIN ADDUCTS
AND
ADDUCT SALTS**

CAS No. 65997-04-8

CAS No. 8050-28-0

CAS No. 68554-16-5

CAS No. 68201-59-2

CAS No. 68649-83-2

CAS No. 85409-27-4

Submitted to the US EPA

By

**The Pine Chemicals Association, Inc.
HPV Task Force
Consortium Registration #**

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Test Plan for Rosin Adducts and Adduct Salts

Summary

The Pine Chemicals Association, Inc. (PCA) is sponsoring 36 HPV chemicals, including 19 members of the rosin family. A test plan for rosin and rosin salts (comprising six substances) has previously been submitted. Rosin esters (comprising seven substances) will be addressed in a subsequent test plan.

This Test Plan addresses the following six chemicals, known collectively as Rosin Adducts and Adduct Salts:

CAS No. 65997-04-8, Rosin, fumarated
CAS No. 8050-28-0, Rosin, maleated
CAS No. 68554-16-5, Rosin, maleated/fumarated
CAS No. 68201-59-2, Rosin, fumarated, sodium salt
CAS No. 68649-83-2, Rosin, fumarated, potassium salt
CAS No. 85409-27-4, Rosin, maleated, potassium salt

All of the members of this group of substances are closely related to rosin, which is a naturally occurring substance found in trees, predominantly pine trees. Rosin is composed primarily of resin acids, a class of tricyclic carboxylic acids, but also contains minor amounts of dimerized rosin, fatty acids and unsaponifiable matter.

The six substances in this subgroup of rosins are all composed of rosin that has been chemically reacted with either fumaric acid or maleic anhydride. Because of the complex nature of their composition, rosin adducts and the rosin adduct salts are considered "Class 2" substances.

The rosin adducts are typically utilized as chemical intermediates which, after undergoing further reactions, have numerous uses. For example, the rosin adducts (i.e., non salts) may undergo reactions such as esterification and polymerization and then can be used in the production of a wide variety of derivatives that go into printing inks and surface coatings. The rosin adducts may also be used to form sodium and potassium adduct salts which are used for sizing paper to improve the final finish of the paper and to provide water resistance.

There are essentially no available SIDS data on rosin adducts or adduct salts. PCA will conduct appropriate physical/chemical property and environmental fate testing on all six substances. PCA has elected to treat this group of chemicals as a category for purposes of the HPV program. Rosin, fumarated (CAS# 65997-04-8) has been selected as the representative substance in this category for ecotoxicity and mammalian toxicity testing.

A brief summary of the available data for the substances in this category, and the anticipated additional testing, is described below in Table 1.

Table 1
Matrix of Available Adequate Data and Proposed Testing
On Rosin Adducts and Adduct Salts *

Chemical and CAS #	Required SIDS Endpoints										
	Partition Coef.	Water Sol.	Biodeg.	Acute Fish	Acute Daph.	Acute Algae	Acute oral	Repeat Dose	In vitro genotox (bact.)	In vitro genotox (non-bact.)	Repro/Develop
65997-04-8, Rosin, fumarated	Test	Test	Adeq.	Test	Test	Test	Test	Test	Test	Test	Test Repro/ Test Develop.
8050-28-0, Rosin, maleated	Test	Test	Test	C	C	C	C	C	C	C	C
68554-16-5, Rosin, maleated/fumarated	Test	Test	Test	C	C	C	C	C	C	C	C
68201-59-2, Rosin, fumarated, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C
68649-83-2, Rosin, fumarated, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C
85409-27-4, Rosin, maleated, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data

Test Indicates proposed testing

C Indicates category read-down from proposed test data on "rosin, fumarated."

***** No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation and transport and distribution between environmental compartments, as explained in the test plan.

Physical/Chemical Properties

Physical and chemical properties will be determined when appropriate. However, many of the physical and chemical properties cannot be measured or the tests are not applicable for these compounds:

- Melting points will not be determined because these substances are complex mixtures and either will not give a sharp melting point when heated or will decompose before they melt.

- Boiling points cannot be determined because these substances are complex mixtures and will decompose before they boil.
- Vapor pressure of these chemicals under ambient conditions is essentially zero and experimental measurement is not possible.
- Water solubility of the compounds in this category will be determined.
- Partition coefficients will be measured for all of the substances in this category. However, the partition coefficient testing likely will yield a range of values representing the various components, rather than a single value representing the mixture.

Environmental Fate

With respect to the SIDS environmental fate endpoints:

- Biodegradation data will be generated for five of the compounds in this category. Data are available for the sixth compound.
- Hydrolysis in water will not be determined for any of the compounds in this category because the members of this category lack a functional group that would be susceptible to hydrolysis in the manner this test was designed to measure.
- Photodegradation is not relevant, since the vapor pressure of these compounds is essentially zero and they could not enter the atmosphere.
- Transport and distribution between environmental compartments will not be determined due to the inability to provide usable inputs to the required model.

Ecotoxicity

- Using fumarated rosin, acute toxicity to fish, daphnia and algae will be tested under conditions that maximize solubility, but reduce exposure to insoluble fractions that may cause nonspecific toxicological effects.

Mammalian Toxicity

- Data on acute toxicity, repeat dose toxicity, genotoxicity, reproductive and developmental effects for fumarated rosin will be generated.

The Pine Chemicals Association, Inc. HPV Task Force includes the following companies:

Akzo Nobel Resins
Akzo Nobel - Eka Chemicals Incorporated
Arizona Chemical Company
Asphalt Emulsion Manufacturers Association
Boise Cascade Corporation
Cognis Corporation
Eastman Chemical Co. (including the former Hercules Inc. Resins Division)
Georgia-Pacific Resins Inc.
ICI Americas (including the former Uniqema)
Inland Paperboard & Packaging, Inc.
International Paper Co. (including the former Champion International Corporation)
Koch Materials Co.
McConaughay Technologies, Inc.
Mead Corp.
Packaging Corporation of America
Plasmine Technology, Inc.
Raisio Chemicals
Rayonier
Riverwood International
Smurfit – Stone Container Corporation
Westvaco
Weyerhaeuser Co.

The Task Force will be filing multiple test plans covering various chemicals. Not all members of the Task Force produce the substances covered by this test plan.

I. Description of Rosin Adducts and Adduct Salts

The Pine Chemicals Association, Inc. (PCA) is sponsoring six HPV chemicals known collectively as Rosin Adducts and Adduct Salts. This group of chemicals consists of the following:

CAS No. 65997-04-8, Rosin, fumarated
CAS No. 8050-28-0, Rosin, maleated
CAS No. 68554-16-5, Rosin, maleated/fumarated
CAS No. 68201-59-2, Rosin, fumarated, sodium salt
CAS No. 68649-83-2, Rosin, fumarated, potassium salt
CAS No. 85409-27-4, Rosin, maleated, potassium salt

All of the members of this group are either fumarated or maleated adducts of rosin (or their salts). Rosin is a naturally occurring substance found in trees, predominantly pine trees. Rosin is composed primarily of resin acids, a class of tricyclic carboxylic acids, but also contains minor amounts of dimerized rosin, fatty acids and unsaponifiable matter. (Rosins and rosin salts are addressed in another test plan.)

A. Composition

Overall, all of the rosin adducts are similar in chemical composition, as all the members of this category are derived from rosin and either fumaric acid or maleic anhydride. (The composition of rosin was described in the PCA's test plan for Rosins and Rosin Salts and the reader is referred to that plan for detailed information.) The sodium and potassium rosin adduct salts are simply the rosin adducts that have been reacted with the appropriate base, either sodium hydroxide or potassium hydroxide. These materials are then dispersed in water for commercial applications.

The reaction between a representative rosin and maleic anhydride is shown schematically in Figure 1. As complex mixtures, rosin adducts and adduct salts are all considered Class 2 substances.

Rosin adducts are made by heating rosin and the adducting reactant together at a temperature of about 200° C. However, the rosin is not completely converted to the adduct form. The commercial adduct consists of a mixture of rosin adducts and rosin with the final ratio a function of the expected use of the product. Because adducts are always prepared with an excess of rosin, the commercial products will not contain any free fumaric acid or maleic anhydride (Zinkel and Russell 1989).

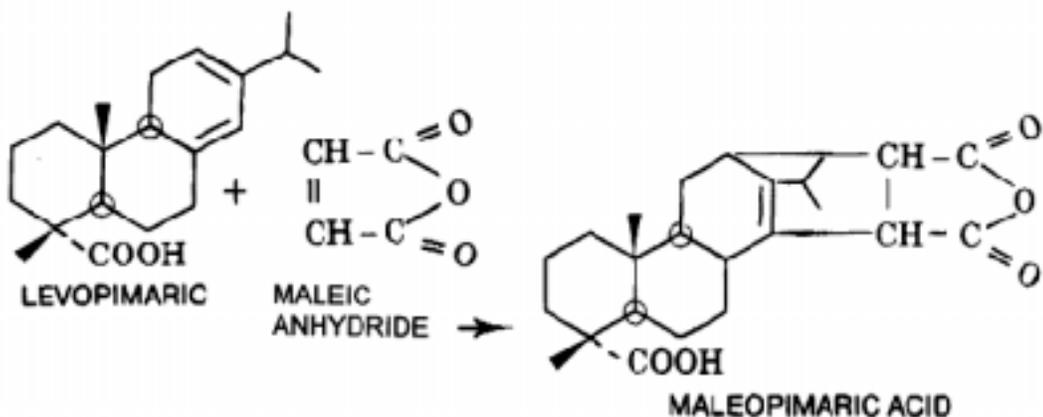


Figure 1. Schematic illustration of the reaction between a representative rosin and maleic anhydride to form a maleated rosin adduct. This reaction, known as a Diels-Alder reaction, requires that both reactants contain double bonds. The reaction product formed between rosin and fumaric acid would be identical to that shown in Figure 1 except that the anhydride group would be open and the resulting carboxyl groups would be in a trans configuration compared to a cis configuration for maleic adducts. That ring would also open when the maleic adduct is converted to a salt.

B. Commercial Uses of Rosin Adducts and Adduct Salts

Fumaric acid or maleic anhydride are commonly added to rosin to increase its softening point, stability, and overall functionality. The rosin adducts are typically utilized as chemical intermediates which undergo further reactions (e.g., esterification and neutralization) to form derivatives that go into printing inks and surface coatings. The sodium and potassium rosin adduct salts are used in paper sizing to improve the final finish of the paper and to provide water resistance. Fortified size (the name given to size containing the adducted material) offers greater efficiencies in the sizing process over unmodified rosin size. A schematic of the production and commercial uses of rosin adducts is shown below in Figure 2.

C. Complexity of Analytical Methodology

All of the substances in this category are Class 2 substances. This, combined with the fact that rosin adducts are essentially insoluble in water and decompose on heating at high temperature, creates a variety of analytical challenges. Gas chromatography of methylated derivatives is the accepted method for the analysis of the members of this category. Based on the method validation work to date, it appears that the analytical procedures will be adequate for the proposed testing.

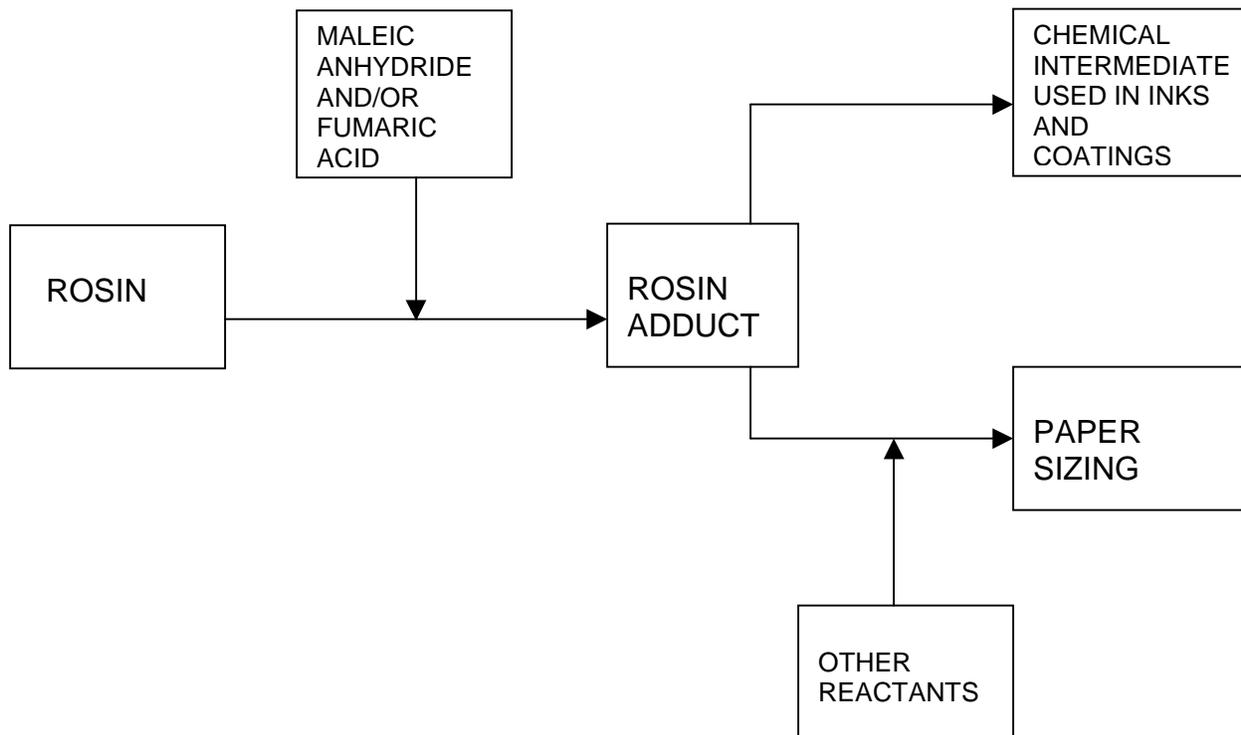


Figure 2. Schematic of rosin adduct production and end use applications

II. Rationale for Selection of Representative Compound for Testing

Rosin, fumarated (CAS# 65997-04-8) has been selected as the representative substance in this category for testing for the applicable SIDS ecotoxicity and mammalian toxicity tests, as shown in Table 2 (identical to Table 1). As further indicated in Table 2, pertinent physical/chemical properties and environmental fate endpoints will be determined for all six members of this category where data are not already available.

Based on an understanding of the chemistry involved in the production of fumarated or maleated adducts of rosin, the selection of fumarated rosin as the most representative substance to be tested is based on the following factors.

- All of the substances in this category are very similar in chemical composition being either fumarated or maleated adducts of rosin or rosin salts.

- The fumarated rosin adduct is the most chemically and thermodynamically stable of the adducts.
- These chemicals meet the “family approach” criterion listed by EPA for grouping related chemicals into a category when they are acids or acid salts. The rosin adduct salts are quickly converted into the free adducts when they are neutralized by acid or by dilution, as would be the case under typical toxicity testing conditions.

In summary, this group of chemicals fits the requirements of the EPA's HPV Challenge Program for a chemical category, and fumarated rosin is the appropriate representative test material from this category.

Table 2
Matrix of Available Adequate Data and Proposed Testing
On Rosin Adducts and Adduct Salts*

Chemical and CAS #	Required SIDS Endpoints											
	Partition Coef.	Water Sol.	Biodeg.	Acute Fish	Acute Daph.	Acute Algae	Acute oral	Repeat Dose	In vitro genotox (bact.)	In vitro genotox (non-bact.)	Repro/ Develop	
65997-04-8, Rosin, fumarated	Test	Test	Adeq.	Test	Test	Test	Test	Test	Test	Test	Test	Test Repro/ Test Develop.
8050-28-0, Rosin, maleated	Test	Test	Test	C	C	C	C	C	C	C	C	C
68554-16-5, Rosin, maleated/ fumarated	Test	Test	Test	C	C	C	C	C	C	C	C	C
68201-59-2, Rosin, fumarated, sodium salt	Test	Test	Test	C	C	C	C	C	C	C	C	C
68649-83-2, Rosin, fumarated, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C	C
85409-27-4, Rosin, maleated, potassium salt	Test	Test	Test	C	C	C	C	C	C	C	C	C

Adeq. Indicates adequate existing data

Test Indicates proposed testing

C Indicates category read-down from proposed test data on “rosin, fumarated”

* No testing will be conducted for melting point, boiling point, vapor pressure, hydrolysis, photodegradation and transport and distribution between environmental compartments, as explained in the test plan.

III. Review of Existing Data and Development of Test Plan

PCA has undertaken a comprehensive evaluation of all relevant data on the SIDS endpoints for the chemicals in this category. No data are available for most of the SIDS endpoints for this category. Table 2 shows data gaps that will be filled by proposed testing.

A. Evaluation of Existing Physicochemical Data and Proposed Testing

The basic physicochemical data required in the SIDS battery includes melting point, boiling point, vapor pressure, partition coefficient (K_{ow}), and water solubility. Some of these measures are inapplicable given the nature of the materials. Moreover, Class 2 substances are composed of a complex mixture of substances and are often difficult to characterize. Rosin adducts and adduct salts are not only Class 2 substances, but also are derived from natural sources. Therefore, their composition is variable and cannot be represented by a single chemical structural diagram. Due to this “complex mixture” characteristic of rosin adducts and related compounds, some physical property measurements, such as partition coefficient, do not give single definitive results because the methodology used to determine these properties will actually fractionate or partition the substance into various components. Consequently, some the results are likely to be erroneous, difficult to interpret, or meaningless.

1. Melting Point

Due to their complex nature, none of the members of this category have a well-defined melting point. These substances soften when heated and so have softening points rather than a true melting point. The softening point of these compounds can cover a wide range depending on the level of adducting reactant in the substance and the type of reactant. Therefore, these substances do not have specific melting points. The adduct salts decompose on heating, and so melting point has no significance for these materials. Consequently, the melting point of these substances will not be measured.

2. Boiling Point

All of the members of this category are produced by high temperature reactions and are non-volatile solids at ambient temperatures. A boiling point under ambient conditions has no significance because these materials will thermally decompose before they boil. Accordingly, measurement of this property is inappropriate for all the substances in this category.

3. Vapor Pressure

Vapor pressures for the rosin adducts (which are solids at ambient temperatures) are effectively zero, and their experimental measurement is inappropriate. In

addition, when rosin adduct salts are dissolved or dispersed in water, their solutions or dispersions will reflect the vapor pressure of the water rather than the salt, and therefore measurement of this property is inappropriate.

4. Water Solubility

The water solubility of the six compounds in this category will be determined using OECD method 105.

5. Partition Coefficient

The partition coefficient (i.e., K_{ow}) for the compounds in this category will be determined using OECD method 107. As noted above, it is likely that a range of K_{ow} values, rather than a single value, will be generated when this endpoint is determined. This outcome reflects the complex nature of Class 2 mixtures.

Summary of Physicochemical Properties Testing: The water solubility and partition coefficients of all of the substances in this category will be determined using OECD methods 105 and 107, respectively. Tests for melting point, boiling point, and vapor pressure are inapplicable to these substances.

B. Evaluation of Existing Environmental Fate Data and Proposed Testing

The fate or behavior of a chemical in the environment is determined by the reaction rates for the most important transformation (degradation) processes. The basic environmental fate data covered by the HPV Program include biodegradation, stability in water (hydrolysis as a function of pH), photodegradation and transport and distribution between environmental compartments.

1. Biodegradation

Biodegradability provides a measure for the potential of compounds to be degraded by microorganisms. Depending on the nature of the test material, several standard test methods are available to assess potential biodegradability.

One of the chemicals in this category (rosin, fumarated) has existing data on the biodegradation endpoint. Biodegradation for the other five substances in this category will be determined. For the adduct salts OECD method 302B will be used and for the non-salts OECD method 301B will be used.

2. Hydrolysis

Hydrolysis as a function of pH is used to assess the stability of a substance in water. Hydrolysis is a reaction in which a water molecule (or hydroxide ion) substitutes for another atom or group of atoms present in an organic molecule. If there is no functional group suitable to be displaced, then the organic compound is considered to be resistant to hydrolysis. None of the substances in this category contains an organic functional group that might be susceptible to this physical degradative mechanism. The maleated rosin adduct will hydrolyze by addition into the acid form, but does not undergo degradation. Therefore, hydrolysis need not be measured.

In addition, low water solubility often limits the ability to determine hydrolysis as a function of pH. The three non-salt rosin adducts have very low solubility in water. Therefore, these materials are expected to be stable in water and it would be unnecessary to attempt to measure the products of hydrolysis. With respect to the rosin adduct salts, in an aqueous medium they hydrolyze (ionize) immediately, but form stable species. Consequently, it is also unnecessary to measure this endpoint for the salts of the rosin adducts.

3. Photodegradation

Due to their lack of any vapor pressure under ambient conditions, there is essentially no opportunity for any of these chemicals to enter the atmosphere. Thus, photodegradation is irrelevant. In addition, based on the constituents in these complex mixtures, there is no reason to suspect that they would be subject to breakdown by a photodegradative mechanism. Consequently, this endpoint will not be determined for any of the substances in this category.

4. Transport and Distribution Between Environmental Compartments

The transport and distribution between environmental compartments is intended to estimate the ability of a chemical to move or partition in the environment. The determination of this property requires the use of various models (e.g., level III model from the Canadian Environment Modeling Centre at Trent University). For Class 2 substances such as the rosin adducts or adduct salts, the required inputs to the model including molecular mass, reaction half-life estimates for air, water, soil, sediment, aerosols, suspended sediment, and aquatic biota are either not available or impossible to determine. In addition, the multiple K_{ow} values typically derived for substances of this complexity as a consequence of sample fractionation reflect various components in the mixture and are not representative of the mixture itself. Consequently, due to the inability to provide usable inputs to the required model, no determination of transportation and distribution between environmental compartments will be undertaken for rosin adducts and adduct salts.

Summary of Environmental Fate Testing: Biodegradation data will be generated for five of the six compounds in this category using OECD method 302B for the salts and OECD method 301B for the non-salts. Photodegradation, hydrolysis and transport and distribution between environmental compartments are not applicable to these chemicals.

C. Evaluation of Existing Ecotoxicity Data and Proposed Testing

The basic ecotoxicity data that are part of the HPV Program include acute toxicity to fish, daphnia and algae. While there are some existing data on these endpoints for one of the substances in this category, the inconsistencies in how water samples were prepared for testing these endpoints render these data inadequate. Consequently, acute toxicity to fish, daphnia and algae will be tested for fumarated rosin under conditions that maximize the solubility under the specific test exposure conditions, but reduce exposure to insoluble fractions, which may cause nonspecific toxicological effects. Initially, the effect of both filtering, to further minimize nonspecific physical effects, and of reducing the pH to the lower end of the acceptable range for test organism survival, will be investigated to determine whether they influence toxicological effects. The results of preliminary tests will be used to select the most appropriate test conditions for the definitive test for each species.

Summary of Ecotoxicity Testing: The acute toxicity of fumarated rosin to fish (OECD 203), daphnia (OECD 202) and algae (OECD 201) will be tested under conditions that maximize solubility, but reduce exposure to insoluble fractions, which may cause nonspecific toxicological effects.

D. Evaluation of Existing Human Health Effects Data and Proposed Testing

1. Acute Oral Toxicity

Acute oral toxicity studies investigate the effect(s) of a single exposure to a relatively high dose of a substance. This test is conducted by administering the test material to rats or mice in a single gavage dose. Harmonized EPA testing guidelines (August 1998) set the limit dose for acute oral toxicity studies at 2000 mg/kg body weight. If less than 50 percent mortality is observed at the limit dose, no further testing is needed. A test substance that shows no effects at the limit dose is considered essentially nontoxic. If compound-related mortality is observed, then further testing may be necessary.

Summary of Available Acute Oral Toxicity Data

There are no acute oral toxicity data for any of the compounds in this category. Consequently, the acute toxicity of fumarated rosin in rats will be determined using OECD method 401.

Summary of Acute Oral Toxicity Testing: Fumarated rosin will be tested for acute oral toxicity using OECD method 401.

2. Repeat Dose Toxicity

Subchronic repeat dose toxicity studies are designed to evaluate the effect of repeated exposure to a chemical over a significant period of the life span of an animal. Typically, the exposure regimen in a subchronic study involves daily exposure (at least 5 consecutive days per week) for a period of not less than 28 days or up to 90 days (i.e., 4 to 13 weeks). The HPV program calls for a repeat dose test of at least 28 days. The dose levels evaluated are lower than the relatively high doses used in acute toxicity studies. In general, repeat dose studies are designed to assess systemic toxicity, but the study protocol can be modified to incorporate evaluation of potential adverse reproductive and/or developmental effects.

Summary of Available Repeat Dose Toxicity Data

There are no existing data on repeat dose toxicity for any of the compounds in this category. Consequently, using OECD method 422, repeat dose toxicity will be determined for fumarated rosin in conjunction with testing for reproductive and developmental effects. Combining the testing in a single protocol will require the use of fewer animals.

Summary of Repeat Dose Toxicity Testing: Fumarated rosin will be tested for repeat dose toxicity (as well as reproductive and developmental toxicity) using OECD method 422.

3. Genotoxicity – In vitro

Genetic testing is conducted to determine the effects of substances on genetic material (i.e., DNA and chromosomes). Mutations of genes can occur spontaneously or as a consequence of exposure to chemicals or radiation. Genetic mutations are commonly measured in bacterial and mammalian cells, and the HPV program calls for completing both types of tests.

Summary of Available Genotoxicity Data

There are no genotoxicity data for any of the compounds in this category. This endpoint will be determined for fumarated rosin in *Salmonella* (OECD 471) and in mammalian cells (OECD 476).

Summary of Genotoxicity Testing: Fumarated rosin will be tested for genotoxicity in bacteria (OECD 471) and mammalian cells (OECD 476).

4. Reproductive and Developmental Toxicity

Reproductive toxicity includes any adverse effect on fertility and reproduction, including effects on gonadal function, mating behavior, conception, and parturition. Developmental toxicity is any adverse effect induced during the period of fetal development, including structural abnormalities, altered growth and post-partum development of the offspring.

The “toxicity to reproduction” aspect of the HPV Challenge Program can be met by conducting a reproductive/developmental toxicity screening test or adding a reproductive/developmental toxicity screening test to the repeat dose study (OECD 421 or OECD 422, respectively).

Summary of Available Reproductive and Developmental Toxicity Data

There are no reproductive or developmental toxicity data for any of the compounds in this category. Consequently, fumarated rosin will be tested for reproductive and developmental toxicity using OECD method 422, in conjunction with testing for repeat dose toxicity. Combining the testing in a single protocol will require the use of fewer animals.

Summary of Reproductive/Developmental Testing: Fumarated rosin will be tested for reproductive/developmental toxicity (as well as repeat dose toxicity) using OECD method 422.

References

Zinkel, D.F. and Russell, J., Eds. 1989. Naval Stores. Production, Chemistry, Utilization. Pulp Chemicals Association, New York.

September 2001