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EDITOR'S PAGE
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Welcome to the December 1997 issue of the Customs Laboratory Bulletin! This is the only issue for 1997, but what an issue it is, with seven articles covering as broad a range of topics as you could imagine.

Please note that this is the last issue of the CLB to be printed in hard copy for distribution to our subscribers. Future issues will be available by visiting our website at <http://www.customs.ustreas.gov/location/labs/bulletin.htm>. If you would like to be alerted to postings of the CLB, please contact the Editor at the E-mail address given below. If you do not have access to the Internet, contact the Editor by mail, telephone, or fax, and arrangements will be made to continue mail delivery of the CLB to you.

Instructions for preparing articles for submission were published in Volume 8, Number 1 (April 1996). For further information on submitting an article, to request a subscription, or to share comments and suggestions on how the Customs Laboratory Bulletin could better serve your needs, please contact the Editor at the following address:

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DETERMINATION OF LAUNDERED MONEY

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INTRODUCTION

Recently the Savannah Customs Laboratory received a request to determine if United States currency seized from a cocaine drug dealer had been "laundered". In this instance, the laundering was literal. The drug dealer had unwittingly decided to bury his ill gotten gains in his garage. Since he happened to live in a very wet area the money began to rot and his millions were destined to become mulch. To clean up his "dirty money", he washed it in his washing machine. At this point U.S. Customs agents stepped in and made a "clean sweep" of the residence. To help their case, the U.S. Customs Agents wanted to prove that the money had indeed been washed. The agent assigned to the case called the Savannah Customs Laboratory and requested assistance in the detection of (1) mildew, (2) cocaine and (3) laundry detergent.

EXPERIMENTAL

Seven fifty dollar bills were submitted for analysis. The bills arrived in a sealed plastic evidence bag. Upon removal and examination, the bills appeared to be quite worn, in fact some were over 35 years old, and had black areas of discoloration prevalent in worn areas (i.e. creases, folds etc). There was a fragrance associated with laundry detergents detected upon removing the bills from their sealed plastic bag.

Detection of Laundry Detergent

In the analysis of this sample the bills were examined under a ultraviolet light to detect optical brighteners which are prevalent in laundry detergents. Each bill was examined under a long wavelength ultraviolet light. Additionally, some bills obtained from a local bank were washed in a laundry detergent containing optical brighteners and then examined for fluorescence. These bills were checked for fluorescence prior to washing and did not fluoresce.

Microscopic Examination For Mildew

Mildew is a common term used to describe a fungus which typically grows under warm, moist conditions. Upon examination under a stereo microscope, the bills had areas of black discoloration. Fibers from these areas were teased onto a microscope slide and wetted with 95% ethanol. They were subsequently stained for one minute with alkaline methylene blue (1). The slide was flooded with distilled water until the absence of color in the wash water was noted. Next, the fibers were counter stained with safranin for 10 seconds and then rinsed as before and air dried. The fibers were examined under a polarizing light microscope at 630X and 1575X magnification.

Analysis for Cocaine

The sample bills and the original plastic evidence bag were analyzed for the presence of cocaine. During the previous analyses, care was taken in the handling of the bills so as not to disturb any particulate matter which may have been clinging to them. The seven sample bills were placed into a clean plastic bag and shaken. The bag was rinsed with four 25-milliliter portions of methanol. The combined methanol rinses were concentrated to 2 milliliters and placed into a crimp seal vial for GC/MS analysis. The original bag the bills were shipped in was also rinsed with four 25-milliliter portions of methanol. The combined methanol rinses were concentrated to 2

milliliters and placed into a crimp seal vial. Finally, the seven sample bills were extracted with 100 milliliters of methanol, and the methanol concentrated to 2 milliliters and placed into a crimp seal vial. The extractions/washings were analyzed on a Hewlett-Packard 5890A Gas Chromatograph with a 5970 Mass Selective Detector and 7376 Autosampler. The following parameters were used in the analysis:

Column: DB-5 30M .25u 5% Phenyl
Initial Temp: 220 C
Initial Time: 1 min
Rate: 10 C/min
Final Temp: 300 C
Final Time: 5 min
Injection Temp: 280 C
Detector Temp: 280 C
Column Flow: 1 ml/min
Total Flow He: 100 ml/min
Split Ratio: 100:1

RESULTS

Detection of Laundry Detergent

Areas of fluorescence were found on all of the bills, with some bills being more fluorescent than others, indicating the presence of optical brighteners which are found in laundry detergent. These areas of fluorescence were photographed using a Sony CCD/RGB Color Video Camera with a macro-lens and a Sony Mavigraph Color Video Printer UP-7100MD at 4 pictures per sheet resolution. The laboratory washed bills had the same fluorescence as the sample bills. As previously noted the bills were checked for fluorescence prior to washing and did not fluoresce.

Microscopic Examination For Mildew

Fungal spores were present in great quantity and rhizome systems had infiltrated the fibers of the bills. Photomicrographs of the fungal components were taken with the Sony CCD/RGB Color Video Camera and Sony Mavigraph Color Video Printer UP-7100MD.

Analysis for Cocaine

Cocaine was not detected in any of the extracted/washed samples. A cocaine standard was analyzed along with the samples and had a retention time of 6.964 minutes.

CONCLUSIONS

It is our opinion, based upon the described analyses, that the seven bills had been laundered. The presence of optical brighteners and mildew and the absence of cocaine was reported to the agent handling the case. The Savannah Laboratory was later notified by the agent, that when confronted with the laboratory results, the drug dealer became very cooperative.

REFERENCES

(1.) Industrial Microbiology; Prescott, S.C. & Dunn, C.G., McGraw-Hill Book Co. Inc., New York, 1940

ACKNOWLEDGMENTS

Thanks to Kathleen Mulligan-Brown for her assistance with the photography.

RUBBER TYPES AND STRUCTURES¹

(Chapter 40, Headings 4001 and 4002)

Leon Farber

U.S. Customs Laboratory, New York, NY

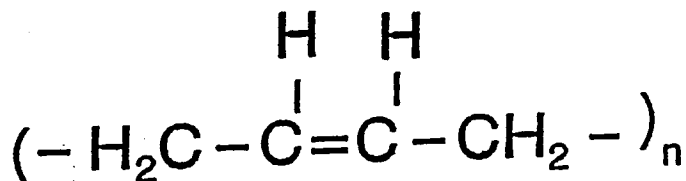
INTRODUCTION

This article comprises a concise overview of rubber structures as presented in Chapter 40, headings 40.01 and 40.02, of the Harmonized System. With only a few exceptions, the format of the article adheres closely to that of Chapter 40. Whenever useful, rubber properties, methods of synthesis and/or uses, are briefly discussed. Bold print is employed solely for the purpose of indicating that the wording was taken directly from the Harmonized System.

This paper is by no means designed to present an exhaustive study of rubber structures, and in some instances, especially when the subheadings refer to the term "other," structures have been omitted. A comparable article, covering Chapter 39, has been published (Farber, Leon, "Polymer Types and Structures," Customs Laboratory Bulletin 6 (2), 53, 1994).

STRUCTURES OF CHAPTER 40

Most of the structures in Chapter 40 are 1,4-polymers. Poly(butadiene), Figure 1,



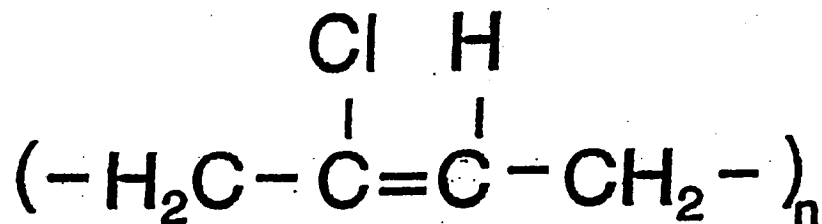
Poly(butadiene)

Figure 1

¹ This article is an updated version of a talk presented at the Rubber Symposium held at the New York Laboratory, August, 1994.

with a repeating unit of four carbon atoms and one double bond is the simplest of the 1,4-polymers in Chapter 40.

Another example of a 1,4-polymer is poly(chloroprene).



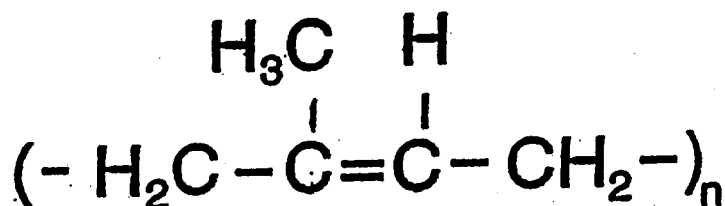
Poly(chloroprene)

Figure 2

The structure of poly(chloroprene) is identical to that of poly(butadiene) with the exception that the proton attached to the second carbon atom of the repeating unit of poly(butadiene) has been replaced by a chlorine atom.

Still another example is poly(isoprene). Here, the proton originally bonded to the second carbon atom of poly(butadiene) has been replaced by a methyl group. Poly(isoprene) is found in nature in both the cis and trans forms. The properties and uses of the two geometric forms are significantly different.

It should be stressed, that in order to be covered by Chapter 40 of the Harmonized System, most of the synthetic rubbers must be unsaturated, and after cross-linking with sulfur, fulfill the stretch requirements of Note 4a. The exceptions will be discussed later.

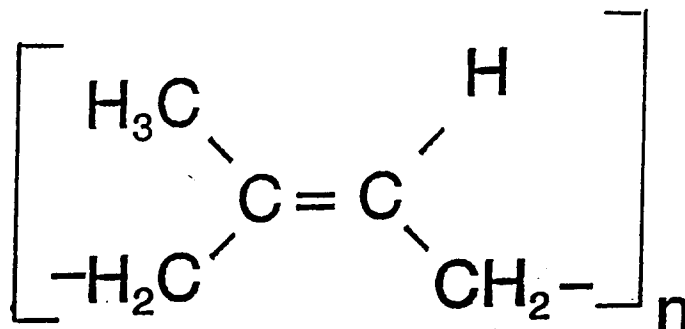


Poly(isoprene)

Figure 3

4001. Natural rubber (NR)

Natural rubber is *cis*-1,4-poly(isoprene).



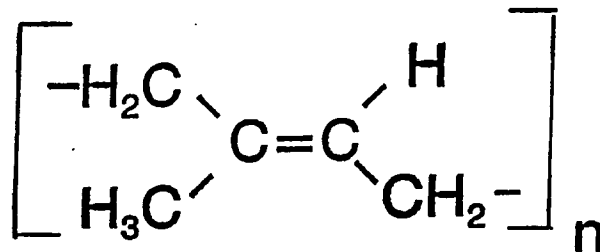
cis-1,4-poly(isoprene)

Figure 4

It is derived predominantly from the rubber tree, *Hevea brasiliensis*. In addition to *cis*-1,4-poly(isoprene) the raw rubber also contains small quantities of proteins, plant sterols, carbohydrates, resin like substances, mineral salts and fatty acids. These other constituents act in part, as accelerators and antioxidants and give the product processing properties which do not exist in the pure hydrocarbon. In order to be of practical use, the raw rubber must be vulcanized (or cross linked). Vulcanization will be discussed later.

Balata, gutta-percha

Both balata and gutta-percha are found in nature as the *trans* form of polyisoprene, Figure 5. Balata is derived from wild bushes and trees, which for the most part, grow along the northeastern coast of South America. Gutta-percha is collected from the trees of the family Sapotaceae, originating in Malaysia, Borneo, and Sumatra.



trans-1,4-poly(isoprene)

Figure 5

Trans-1,4-polyisoprene is a tough horny material at room temperature, but is soft and tacky at 100°C. It is soluble in most aliphatic hydrocarbons, but is insoluble in aromatic hydrocarbons and most chlorinated hydrocarbons. It is used in the manufacture of golf ball covers, submarine cables and for the preparation of temporary dental fillings.

Both the *cis* and *trans* forms of polyisoprene can be prepared synthetically and will be discussed below, under heading 40.02.

4002. Synthetic rubber Isoprene rubber (IR)

Depending on the catalyst and conditions used, isoprene can be polymerized into either *cis*-1,4-polyisoprene, Figure 6, equation 1, or *trans*-1,4-polyisoprene, Figure 6, equation 2.

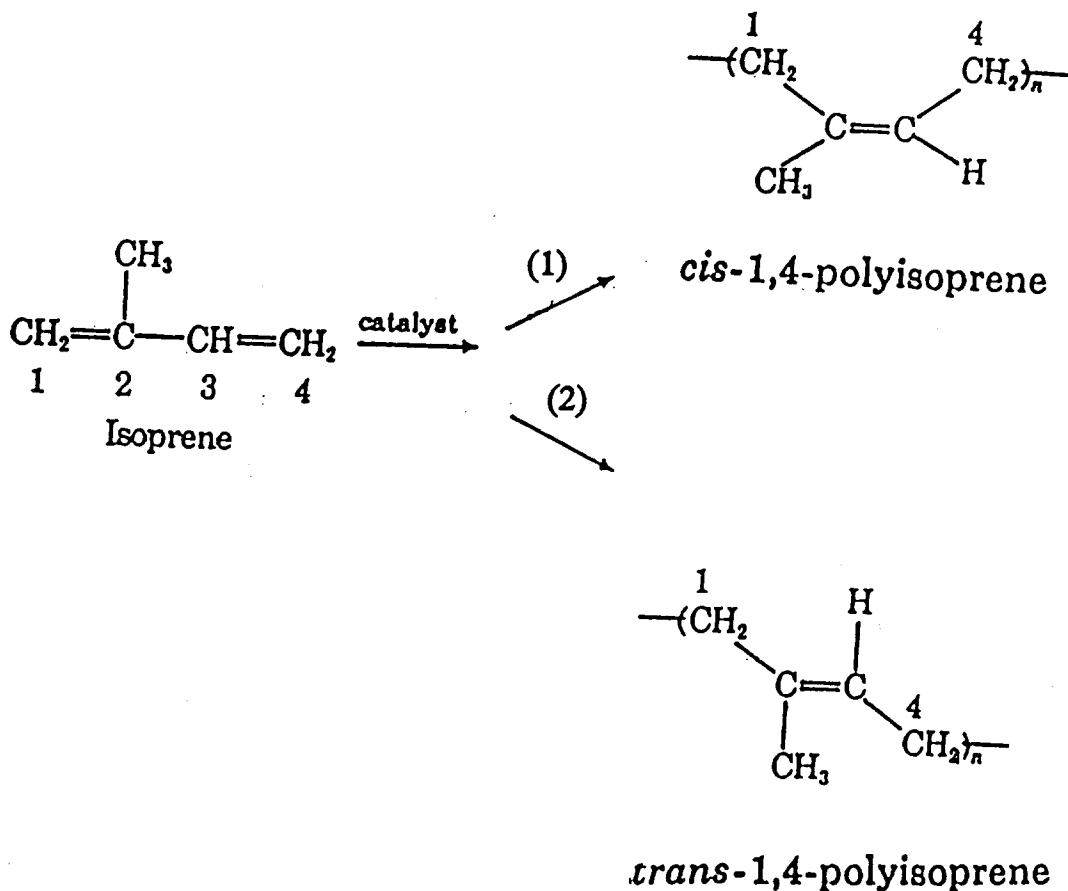


Figure 6

Difficulty in synthesizing *cis*-1,4-polyisoprene was encountered by early chemists; the polymers they prepared consisted of a mixture of isomers and therefore, lacked the desirable properties of natural rubber. During World War II, with natural rubber in short supply, the U.S. Government initiated an intensive research effort to synthesize polyisoprene. The effort failed. A styrene-butadiene copolymer was used as a substitute. The latter polymer will be discussed later.

The breakthrough finally came in 1954. Using the newly developed Ziegler-Natta catalysts, the BF Goodrich Company reported success in developing polyisoprene with a *cis*-1,4-structure of 98%. The catalysts consisted basically of a combination of aluminum alkyl (R_3Al) and titanium tetrachloride ($TiCl_4$). Later, the Firestone Tire and Rubber Company reported the synthesis of polyisoprene with a 92% *cis*-1,4-structure, using organolithium catalysts (RLi).

Among the many uses of the synthetic *cis* polymer is the manufacture of tires, automotive bushings, belting, footwear, adhesives, sheeting, baby bottle nipples, and pharmaceutical sundries.

The preparation of *trans*-1,4-polyisoprene (Figure 6, equation 2) is usually brought about with the use of a mixed catalyst consisting of VCl_3 , $TiCl_3$, and R_3Al . The *trans* polymer (synthetic Balata), has high hardness and tensile strength. It is used primarily for the manufacture of golf ball covers. Among its other uses are hot-melt adhesives, orthopedic splints and temporary fillings for teeth.

Butadiene rubber (BR)

Butadiene rubber ranks second in production among synthetic rubbers, and is surpassed only by that of styrene-butadiene rubber. It is synthesized by addition polymerization, Figure 7.

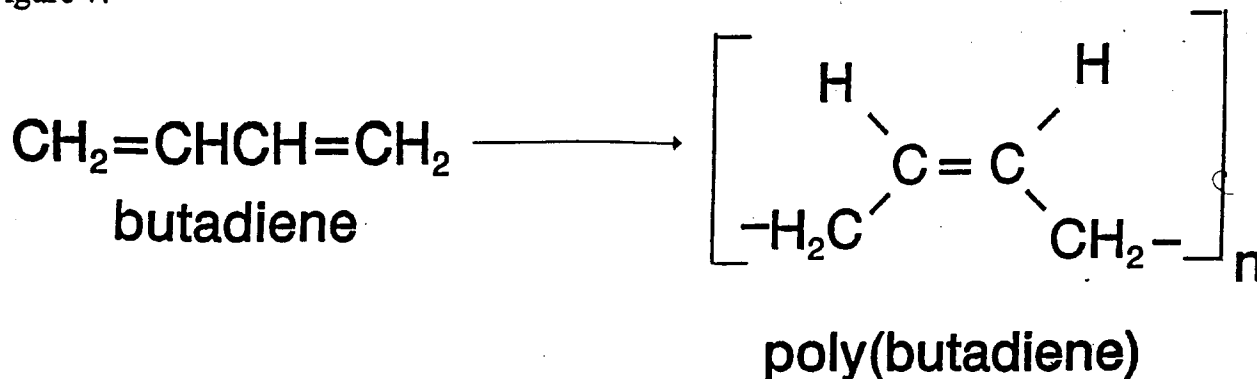


Figure 7

Most commercial polybutadienes are predominantly of the *cis*-1,4 type, and are prepared

using organometallic catalysts. They are in some ways superior to natural rubber because of high abrasion resistance, excellent heat resistance, low temperature performance, and high resilience. Their uses include the manufacture of tire tread compounds, conveyor belts, and blends with natural and styrene-butadiene rubber.

Styrene-butadiene rubber (SBR)

Styrene-butadiene rubber, Figure 8, is the most important synthetic rubber and represents more than half of all synthetic rubber produced. It is a copolymer of 1,3-butadiene and styrene, Figure 8.

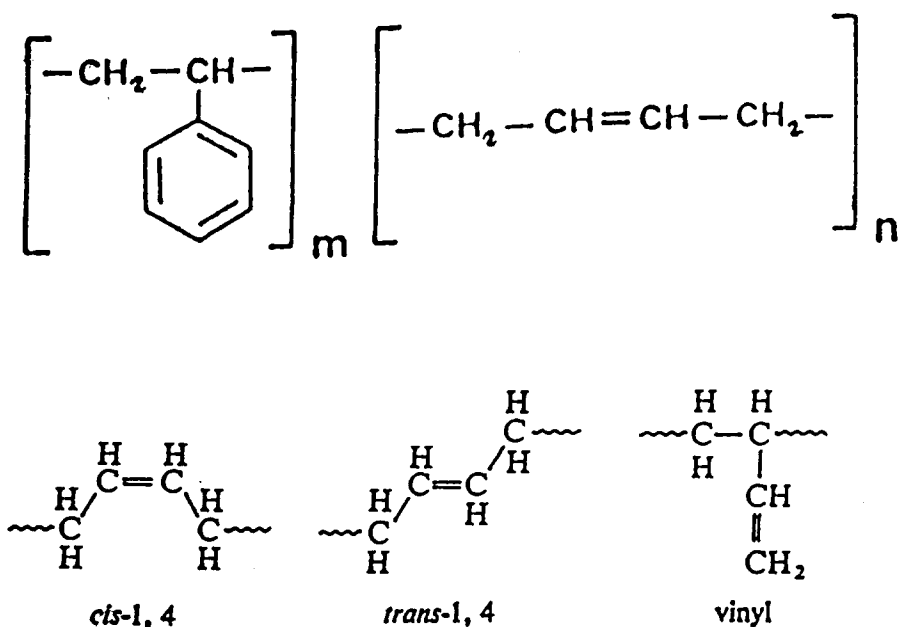
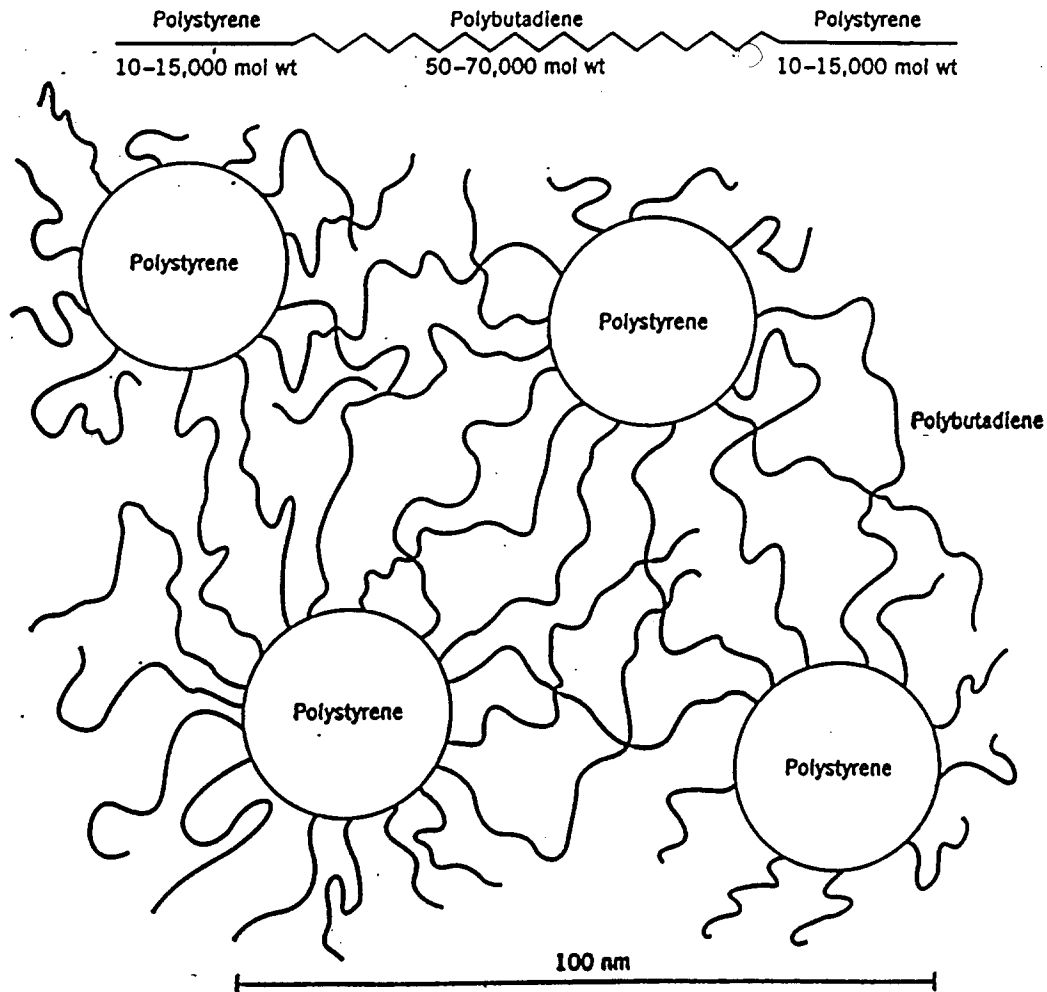


Figure 8

The elastomer can be prepared in either emulsion systems, using a free radical mechanism, or in solutions, using organolithium initiators. Both methods usually result in a rubber containing approximately 23% styrene. In emulsion SBR, styrene is randomly dispersed with butadiene, and the quantities of the unit structures of butadiene are about 65% trans, 18% cis, and 17% vinyl (see Figure 8). Both random and block polymers can be produced from solution systems, and have lower trans, slightly lower vinyl, and higher cis quantities than emulsion SBR.

The major use for styrene-butadiene rubber is in the manufacture of passenger tires and tire products. It is also used to produce, among other items, adhesives and chewing gum.

Using organolithium initiators, as mentioned above, thermoplastic elastomers, of the type shown in Figure 9, can be prepared.



Thermoplastic elastomer of styrene-butadiene rubber.

Figure 9

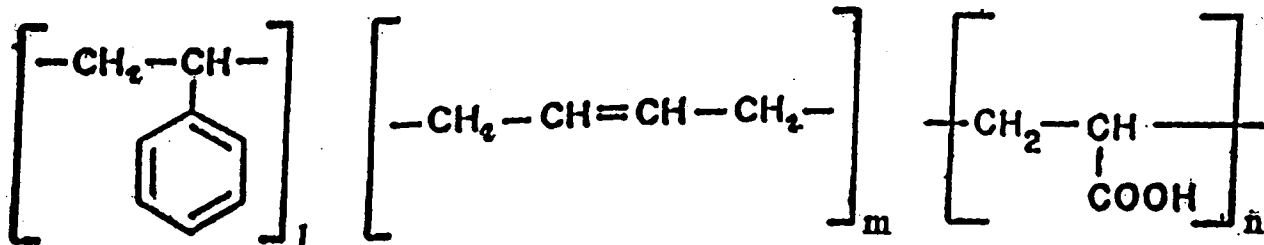
A thermoplastic elastomer is a material that combines the processability of a thermoplastic with the performance of a thermoset rubber. As demonstrated in the example depicted in Figure 9, this type of copolymer consists of a multiphase composition, in which the phases are intimately dispersed. One phase consists of a material that is hard at room temperature, but is fluid upon heating. In Figure 9, the

polystyrene phase is an example of this. The other phase, in this case polybutadiene, is a softer rubberlike material at room temperature. With this kind of structure, the copolymer can be processed as a melt at a relatively low temperature and then cooled to a rubberlike object at room temperature. Unlike thermoplastic elastomers, conventional rubbers, in order to be useful, must be vulcanized (crosslinked) and are therefore thermosetting, and not thermoplastic. Thermoplastic SBR is used in the manufacture of adhesives, footwear and mechanical goods.

As has already been pointed out, thermoplastic elastomers, like most other synthetic rubbers, must have at least one double bond, and after cross-linking with sulfur (vulcanization), fulfill the stretch requirements of Note 4a. The exceptions will be discussed later.

Carboxylated styrene-butadiene rubber (XSBR)

Carboxylated styrene-butadiene rubbers are terpolymers synthesized from styrene, butadiene, and an unsaturated carboxylic acid, usually acrylic or methacrylic acid, Figure 10. Generally, in order to maintain the elastomeric properties of the terpolymer, the quantity of the carboxylic monomer is kept to less than 6%. It is used in carpet backings.



Styrene-butadiene-acrylic acid terpolymer

Figure 10

Isobutene-isoprene (butyl) rubber (IIR)

Butyl rubber is a 1,4 copolymer synthesized by the addition polymerization of isobutylene and 0.5 to 2.5 mole percent isoprene, Figure 11. The presence of the double bond, its ability to be cross-linked with sulfur, and its subsequent exhibition of the elasticity requirements of Note 4a, permit it to be classified as a synthetic rubber in Chapter 40. If isobutylene is polymerized without isoprene, a saturated polymer, poly(isobutylene) results, Figure 12. Being fully saturated, it lacks the required double

bond and is therefore classified in Chapter 39. (See page 56, Customs Laboratory Bulletin 6 (2), 1994.)

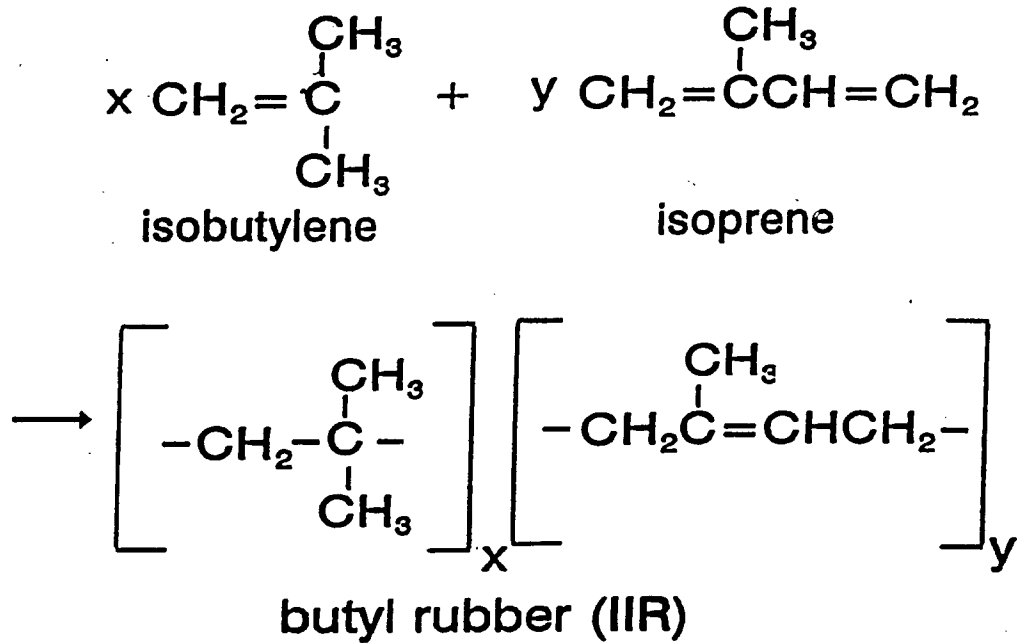
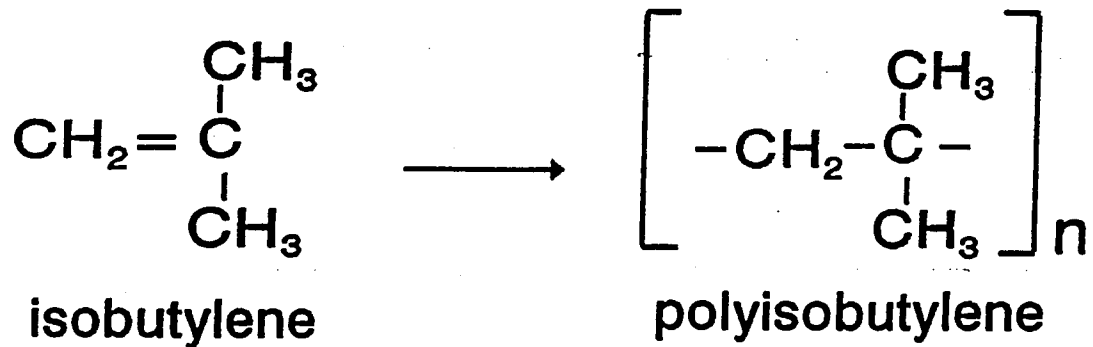


Figure 11



Not classified in Chapter 40

Figure 12

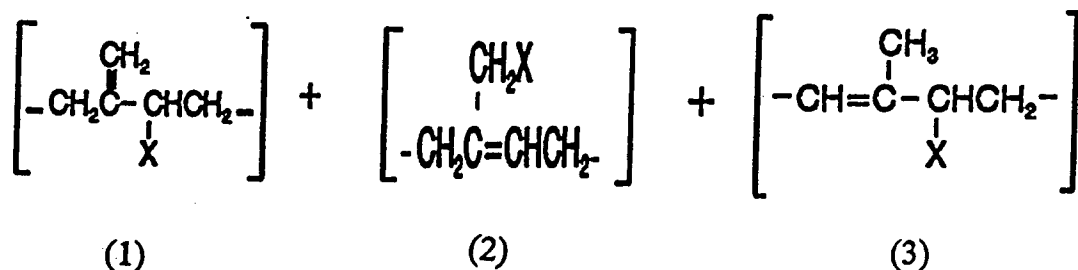
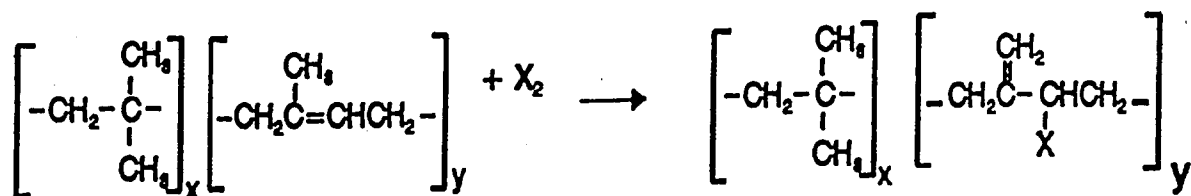
Butyl rubber, with its low level of unsaturation, has a lower permeability to gases and a higher stability to ozone and oxygen attack, than either natural or styrene-butadiene rubber.

It is used for the manufacture of inner tubes, inner linings of tubeless tires, hose for steam

and chemicals, conveyor belts for use with hot articles, sealing materials, rubberized textiles and similar items.

Halo-isobutene-isoprene rubber (CIIR or BIIR)

The halobutyl rubbers, both chlorobutyl (CIIR) and bromobutyl (BIIR), are commercially the most important butyl rubber derivatives. They are prepared by reaction of small quantities of elemental chlorine or bromine with butyl rubber. The reaction and the resulting structures are shown in Figure 13. Halogenation occurs at the isoprene



X = Cl or Br

Figure 13

part of the copolymer and leads to a shift of the double bond. Studies employing nmr indicate that structure 1 predominates.

Like the parent butyl rubber, the halogenated rubbers have low permeability to gases and are resistant to environmental attack. They have, however, greater cure versatility and are able to crosslink in blends with highly unsaturated elastomers

They are used in the manufacture of tire inner liners, sidewalls, and cover strip compounds. Since chlorobutyl rubber can be cured with nontoxic materials, it can be used in products which will contact food.

Chloroprene (chlorobutadiene) rubber (CR)

Polychloroprene was developed in 1927 by chemists from Du Pont, and was the first commercially successful synthetic elastomer. It is also known under the name Neoprene. The rubber is prepared by 1,4-addition polymerization of the chloroprene monomer, Figure 14. The polymer is predominantly in the trans form.

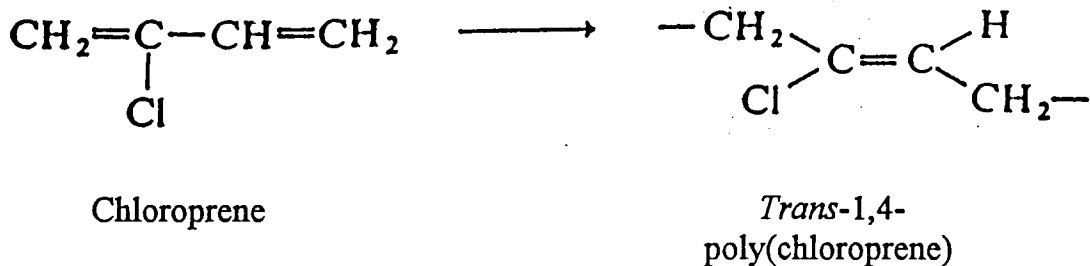


Figure 14

Unlike many other rubbers, poly(chloroprene) is not vulcanized commercially by means of sulfur. Instead, use is made of the fact that the chlorine atoms on the chain can react to some extent with active metals or metal oxides. Zinc oxide and magnesium oxide are used to combine with some of the chlorine and crosslink the polymer chains. Among the many uses of poly(chloroprene) are the manufacture of molded and extruded goods, adhesives, hose, tires, heels and soles, coated fabrics and gaskets.

Acrylonitrile-butadiene rubber (NBR)

Acrylonitrile-butadiene rubber, also referred to as nitrile rubber, is synthesized from 1,3-butadiene and acrylonitrile, Figure 15. The composition of acrylonitrile in commercial

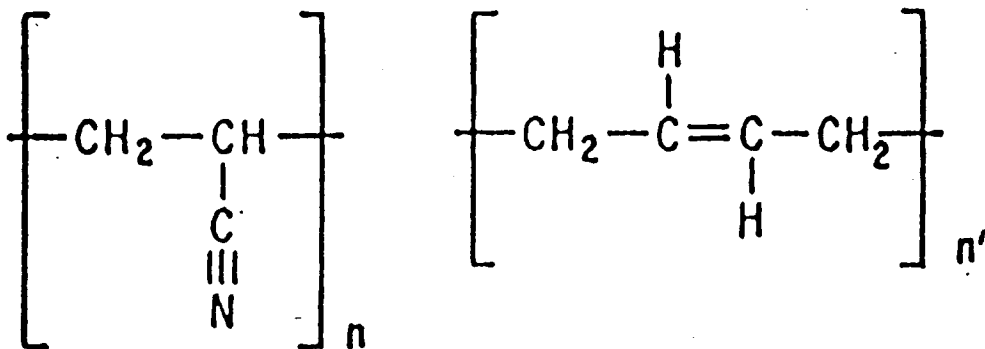


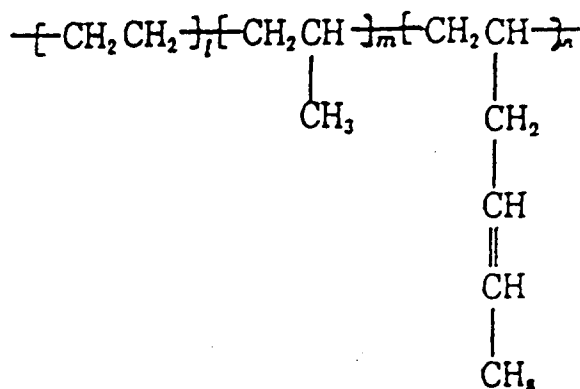
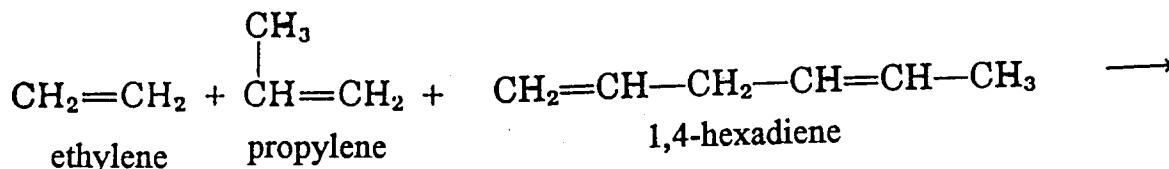
Figure 15

nitrile rubbers, varies from 15 to 50% with 33% being the most common. Butadiene is mostly in the trans form.

With the exception of the thioplasts, to be discussed later, nitrile rubber is the most solvent resistant of all of the synthetic rubbers. Classified as a specialty rubber, it is well known for its resistance to various oils, fuels and chemicals. It is used in the manufacture of seals, gaskets, hose, electrical insulation and the like.

Ethylene-propylene-nonconjugated diene rubber (EPDM)

Ethylene-propylene-nonconjugated diene rubbers are terpolymers synthesized from the monomers, ethylene, propylene, and a nonconjugated diene. The quantity of the nonconjugated diene is usually about 4 to 5% by weight, although it may go as high as 10%. A good example of this type of synthetic rubber is poly(ethylene-co-propylene-co-1,4-hexadiene), Figure 16.



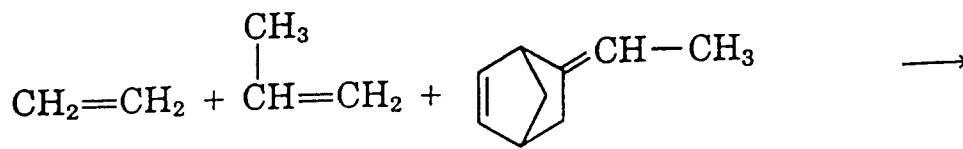
Poly(ethylene-co-propylene-co-1,4-hexadiene)

Figure 16

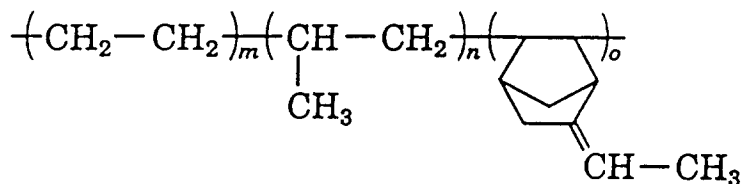
Efforts to introduce conjugated dienes, such as butadiene or isoprene, have been unsuccessful. The catalysts and polymerization conditions which are essential for the manufacture of the random copolymer of ethylene and propylene, will not, at the same time, tolerate a conjugated diene and cause it also, to be included in the molecule.

As can be seen in Figure 16, the remaining double bond is situated in the appendage of the polymer and is not part of its backbone. The outstanding ability of this elastomer to resist attack by heat, light, oxygen and ozone, is attributed to the saturation of its backbone. Any degradation of the unsaturated appendage, will not effect the integrity of the polymer itself. The remaining double bond is available for sulfur vulcanization.

Another example of an EPDM rubber is poly(ethylene-co-propylene-co-ENB), Figure 17.



ethylene propylene ethylidene norbornene
(ENB)



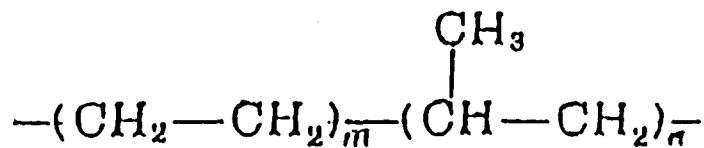
poly(ethylene-co-propylene-co-ENB)

Figure 17

As in the previous example, the unreacted double bond is external to the polymer chain and can be subjected to sulfur vulcanization.

Among the applications of EPDM elastomers are the manufacture of car bumpers, hoses, seals, and wire and cable insulation. It is also used in blends with general purpose rubbers in order to increase their resistance to ozone attack.

If the diene is omitted and ethylene is copolymerized with propylene only, the resulting product is ethylene-propylene copolymer, Figure 18. Being fully saturated it is excluded from Chapter 40 and is in fact classified in Chapter 39. (See page 55, Customs Laboratory Bulletin 6(2), 1994.)



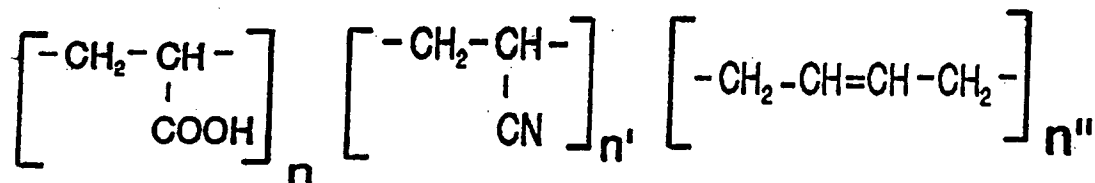
Ethylene-propylene copolymer
Not classified in Chapter 40

Figure 18

Other

Carboxylated acrylonitrile-butadiene rubber (XNBR)

The chain structure of this elastomer is similar to that of nitrile rubber (see Figure 15), with the exception that carboxyl groups are distributed along the chain with a frequency of one to every 100 to 200 carbon atoms. Since this terpolymer contains both double



Carboxylated acrylonitrile-butadiene rubber

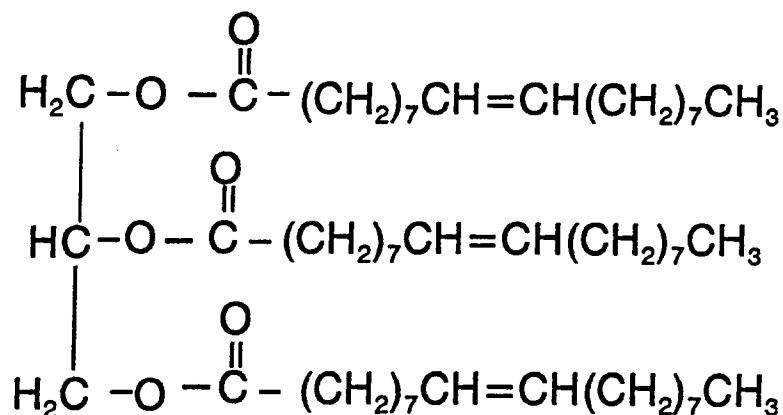
Figure 19

bonds and carboxylic acid groups, it can be crosslinked either by conventional sulfur vulcanization, or by reacting the carboxylic acid groups with a polyvalent metallic ion.

Other (continued)

Factice

Factice is the polymerized product of vegetable and animal oils with sulfur or sulfur monochloride, Figure 20. Rape seed oil is commonly used, but other oils such as linseed, soya bean, and whale oil are also employed. The so called "cold vulcanization" method, is brought about by treating the vegetable oils with 15 to 25% sulfur monochloride at about room temperature. The reaction is exothermic and hydrochloric acid is liberated. The product is white or light yellow in color. Dark factice is made by heating either vegetable or animal oil with sulfur, at a temperature of about 150° C. The product is light brown to dark brown in color.



glyceryl trioleate

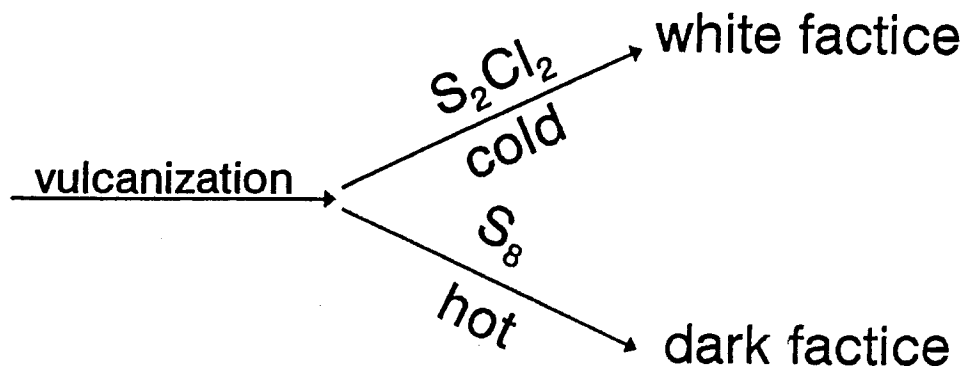


Figure 20

Other (continued)

Factice has very poor abrasion resistance, and for this reason serves very well in pencil erasers. It is also used as a processing aid in compounding natural and synthetic rubbers and for its ability to absorb and retain large quantities of plasticizers in very soft rubbers, such as inking rollers in printing.

Thioplasts (TM)

According to the Explanatory Notes to the Harmonized System, Chapter 40, thioplasts "are saturated synthetic substances, obtained by the reaction of aliphatic dihalides with a sodium polysulphide***." It is important to note that the Explanatory Notes of Chapter

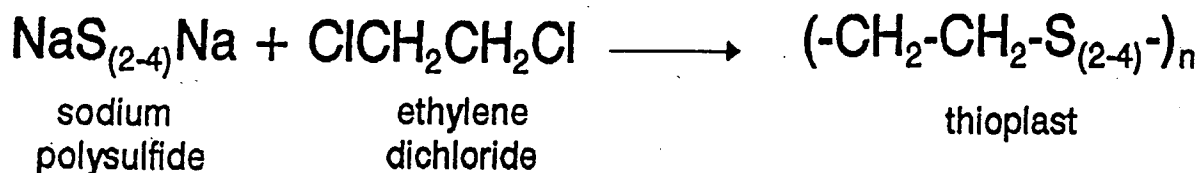


Figure 21

39, distinguishes between "thioplasts," which are classified in Chapter 40, and "polysulphides," a Chapter 39.11 item. "Polysulphides are polymers characterized by the presence of monosulphide linkages in the polymer chain, for example polyphenylene sulphide. In polysulphides each sulphur atom is bound on both sides by carbon atoms, as opposed to the thioplasts of Chapter 40, which contain sulphur-sulphur linkages."

Thioplasts are usually prepared by reacting bis(2-chloroethyl)formal with sodium polysulfide, Figure 22.

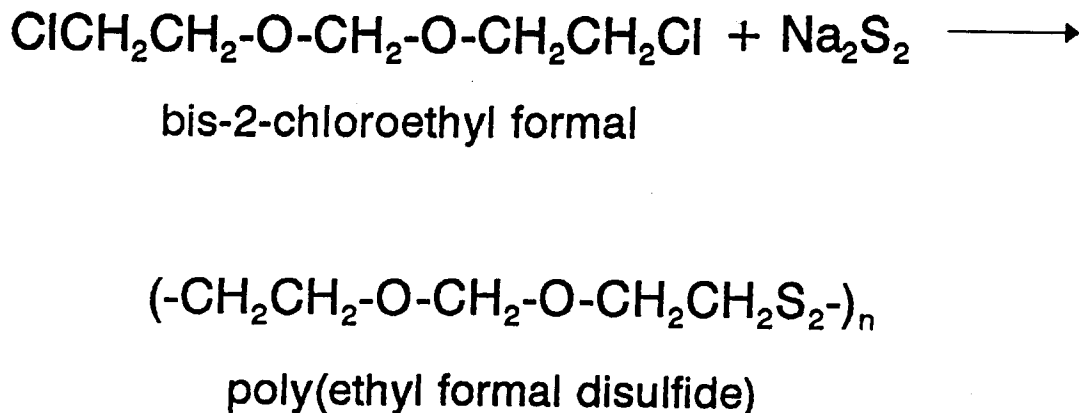


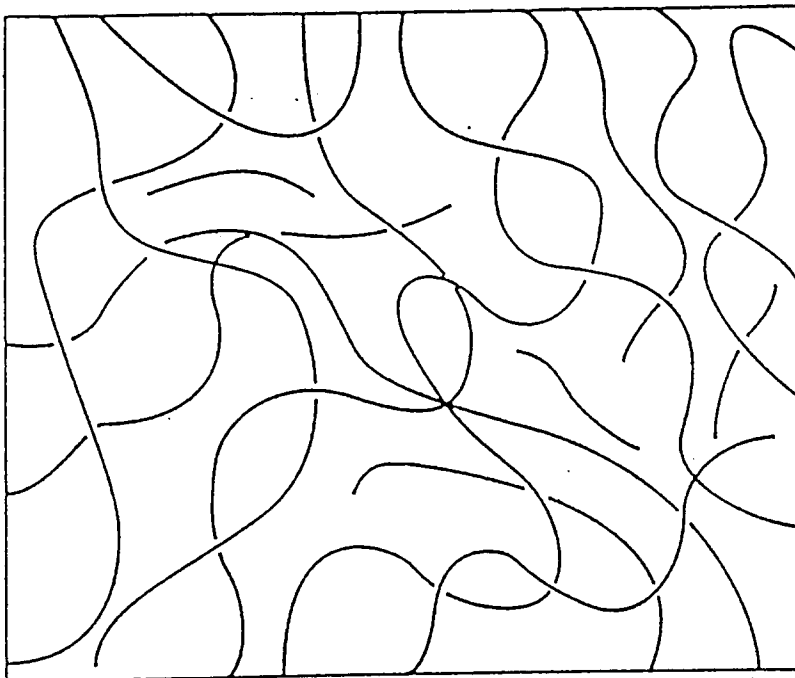
Figure 22

Thioplasts have greater solvent resistance than either natural or conventional synthetic rubbers. This is due to a backbone structure with short carbon sequences interspersed with formal and S_x in contrast to longer hydrocarbon structures found in traditional rubbers. They generally have poor mechanical properties, however. Although they are usually fully saturated, they are included by Note 4b in this Chapter. Thioplasts are produced in both solid and liquid forms.

Vulcanization

The Dictionary of Rubber by K. F. Heinisch, defines vulcanization as, "The conversion of rubber from a predominantly plastic to an elastic condition by three dimensional cross-linking." According to the Explanatory Notes of Chapter 40, "It should be noted that the criterion concerning vulcanization with sulfur is relevant only for the purposes of Note 4, i.e., for determining whether a substance is synthetic rubber or not. Once a substance has been determined to be a synthetic rubber, products made therefrom are considered as vulcanized rubber products for the purpose of headings 40.07 to 40.17, whether they have been vulcanized with sulfur or some other vulcanizing agent."

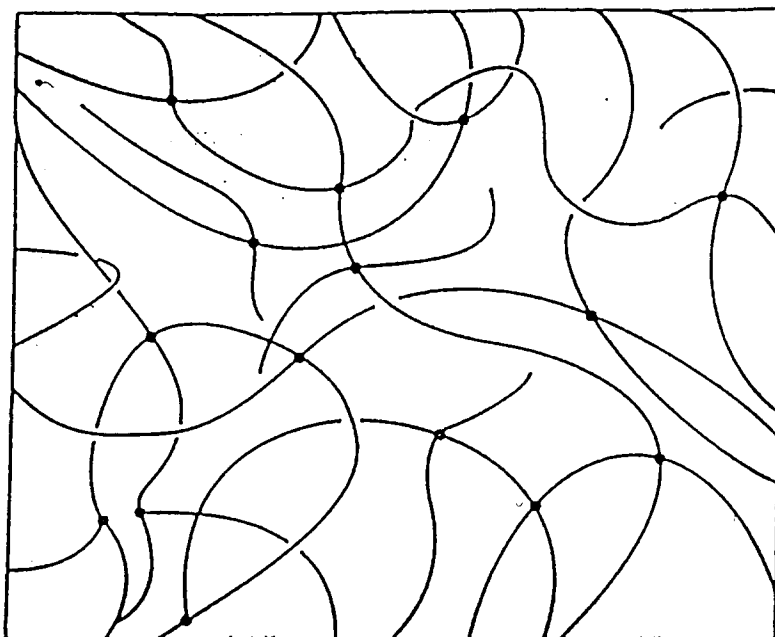
An elastomer before vulcanization is depicted in Figure 23, and after vulcanization in



Unvulcanized Elastomer

Figure 23

Figure 24. When exposed to a distorting force, the chains of an unvulcanized elastomer

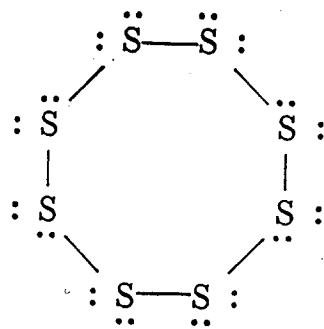


Vulcanized Elastomer

Figure 24

tend to slide past each other, and cannot readily return to their original form when the distorting force is removed. After vulcanization, the polymer chains become fixed and will more readily retract to their original form. Once a rubber has been vulcanized, it becomes elastic, and its form becomes fixed. For this reason, a product is vulcanized only after it is in its final form.

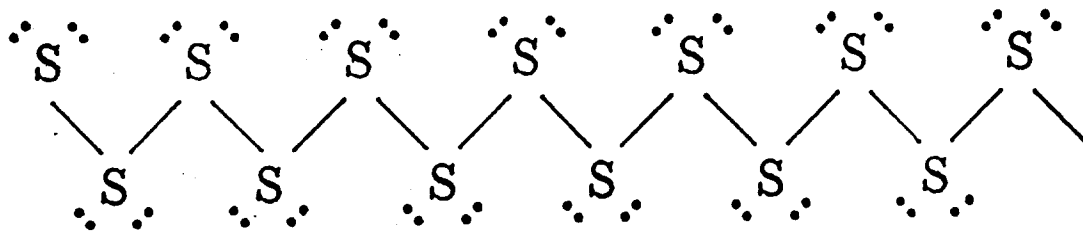
Sulfur vulcanization is generally used commercially for most of the highly unsaturated rubbers. For the most part, rhombic sulfur, Figure 25, is used. For some rubbers it is



Rhombic Sulfur

Figure 25

advantageous to use amorphous sulfur, Figure 26, either alone or in combination with rhombic sulfur.



Amorphous Sulfur

Figure 26

Vulcanization is accomplished by cross-linking reactions involving allylic hydrogen or halogen sites. Cross-linking with sulfur is represented in Figure 27.

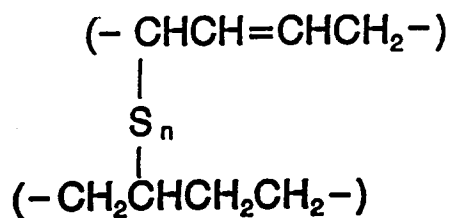
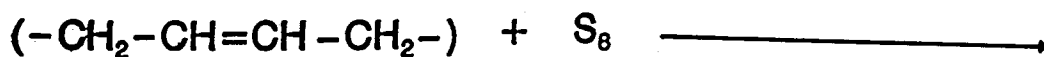
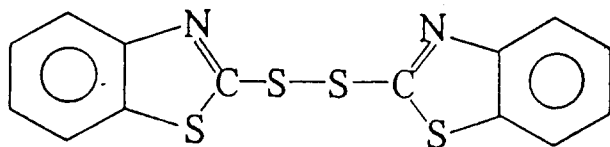
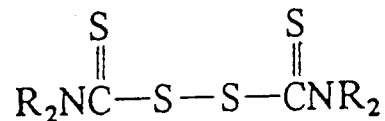


Figure 27

Vulcanizations with sulfur alone are slow and inefficient. Sulfur vulcanizations are carried out commercially in the presence of accelerators and activators. The use of accelerators increases the rate and efficiency of these reactions. Of the many accelerators that are available, two examples are shown in Figure 28. The effectiveness of the accelerators are enhanced by the addition of activators. A combination of zinc oxide and stearic acid are among the most commonly used activators, Figure 29. The zinc is converted to a more soluble form by having the zinc oxide react with stearic acid and forming the zinc salt.



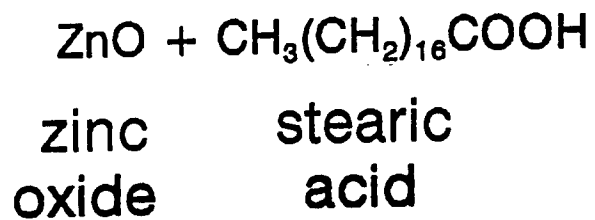
2,2'-dithiobisbenzothiazole



alkylthiuram disulfide

Vulcanization accelerators

Figure 28



Vulcanization activator

Figure 29

REFERENCES

Explanatory Notes to the Harmonized Commodity Description and Coding System, Second ed., Brussels, Belgium: Customs Cooperation Council, 1996.

Farber, Leon, Polymer Types and Structures, Customs Laboratory Bulletin 6 (2), 53, 1994.

Harmonized Tariff Schedule of the United States, Washington, DC: United States International Trade Commission, 1997.

Heinisch, K.F., Dictionary of Rubber, New York, NY: Van Nostrand Company, Inc., 1974.

Kroschwitz, Jacqueline, I., exec. ed., Concise Encyclopedia of Polymer Science and Engineering, New York, NY: John Wiley & Sons, Inc., 1990.

Mark, Herman, F., et. al., ed., Kirk-Othmer Encyclopedia of Chemical Technology, Third and Fourth ed., New York, NY: John Wiley & Sons, Inc., 1978 and 1996.

Mark, Herman F., et. al., ed., Encyclopedia of Polymer Science & Engineering, Second ed., New York, NY: John Wiley & Sons, Inc., 1985.

Morton, Maurice, Rubber Technology, Second ed., New York, NY: Van Nostrand Reinhold Company, Inc., 1973.

Odian, George, Principles of Polymerization, New York, NY: John Wiley & Sons, Inc. 1981.

Sax, Irving, N., and Lewis Sr., Richard J., Hawley's Condensed Chemical Dictionary, Eleventh ed., New York, NY: Van Nostrand Reinhold Company, Inc., 1987.

Ginsenoside Profile of North American and Asian Ginseng

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ABSTRACT

Ginseng is the most widely used medicinal herb in eastern Asia, particularly in the Pacific Rim countries. The North American ginseng has a cooling and calming effect whereas its Asian counterpart has a warming and energizing effect. The North American root commands a higher price than the Chinese ginseng. Fraudulent substitution of the North American variety with the relatively inexpensive Chinese ginseng has been reported. By examining the ginsenoside profile obtained by High Performance Liquid Chromatography (HPLC), we can authenticate ginseng and differentiate between the two varieties in the root form as well as in the processed form.

INTRODUCTION

Ginseng is a deciduous plant belonging to the genus *Panax*. It's believed that *Panax* is an adaptation of the word panacea, in recognition of the oriental perception of the herb. Botanically, the North American ginseng is *Panax Quinquefolius*. The Asian ginseng is *Panax Ginseng*.

Typical of deciduous plants, ginseng undergoes an annual cycle of "death" or dormancy in the winter, when the plant drops its foliage. This is followed by a period of "rejuvenation" in the spring, characterized by the resumption of foliar production and above-ground growth. This annual cycle of rejuvenation or life-after-death and the often humanoid shape of the root adds to the mystique of ginseng as a holistic therapeutic agent and contributes to its use in folklore as an emergency drug to *rejuvenate* the dying¹.

The ginseng plant flowers from about June to July. Small green flowers lead to red berries which ripen to form seeds for future generations. Ginseng roots are harvested between August to September at about the sixth or seventh year. At this point, the average weight of the root is about 200 grams. However, the weight of roots can vary depending on soil fertility

and climatic conditions.

In the wild, ginseng thrives under the shady canopy of hardwood forests. The ginseng plant requires shade, moisture, and a sustained period of winter chill. Temperatures of -5°C to 5°C are needed to induce a period of dormancy. Annual rainfall of 50-100 cm provides sufficient moisture. The map in Figure 1 shows parts of the world where ginseng is found. Note the concentration of ginseng occurring in the northern hemisphere of eastern North America and eastern Asia. This bicentric phytogeographic distribution suggests a close floristic relationship of the eastern sides of the two continental masses in the northern hemisphere². The dotted areas of the map meet the temperature requirements, but generally lack the sufficient rainfall for ginseng to thrive.

North American ginseng is cultivated in Canada with major production centers in Vancouver and Ontario. Wisconsin produces the bulk of the U.S. commercial crop. The Asian ginseng is cultivated in China, particularly the Jilin Province in Manchuria, the Koreas, and other parts of eastern Asia. The North American crop is exported to Asia, through Hong Kong, for processing. A portion of the processed ginseng is then returned to North America for the occidental consumer; the remainder staying in Asia for the oriental market. In Hong Kong, North American ginseng has been reported to command a price 10 times that of the Chinese white ginseng. It is common to find Asian ginseng falsely labeled and retailed as American ginseng in the Orient³.

The ginseng root contains about 70-80% carbohydrate, 9% protein, 5% fiber, and from 2 to 5% *ginsenosides*. The leaf, bud and flower contain higher levels of ginsenosides than the root. However, it is ginseng root that is usually dispensed by apothecaries for medicinal use, while the leaf is primarily used for brewing teas¹.

Ginsenosides are triterpenoid saponins. As triterpenoids, the basic chemical structure of ginsenosides contain 30 carbon atoms (Figure 2). As saponins, ginsenosides are natural compounds that cause foaming or frothing in aqueous solutions when agitated. Ginsenosides are glycosides, with sugar molecules attached to a tetracyclic backbone. Glycosides are hydrolyzed by acids to yield aglycones or sapogenins and constituent sugars. The tetracyclic sapogenin structure of ginsenosides resemble steroids (Figure 3). Many believe that this structural similarity supports the view that ginsenosides possess therapeutic steroidal properties and are the class of biologically active compounds in ginseng.

The word "gin-seng" is translated as "the essence of man." For thousands of years, the Asian people have used it as a tonic, as well as an emergency medicine to rescue the dying. The wealthy use it as a rejuvenating and revitalizing agent. In the West, ginseng is used to improve stamina, mental acuity, and general resistance to stress and disease. Historical descriptions suggest daily administration of ginseng to restore the yin and yang and increase the longevity of men and women¹.

EXPERIMENTAL

A 20g sample of sliced ginseng root is refluxed in 150mL of water (18 megohm purity, Millipore Corp. Milford, MA) for 1.5 hours. The extract is allowed to cool, and a 3 mL aliquot is passed through a pre-conditioned C18 Sep-Pak cartridge (Waters Associates, Milford, MA). The cartridge is washed with 5 mL of water, and the ginsenosides eluted with 3 mL of methanol (J.T. Baker HPLC grade, VWR Scientific Products, San Francisco, CA). This extract is then filtered through a nylon membrane sample filter (National Scientific Company, Lawrenceville, GA) and analyzed by HPLC.

Processed ginseng preparations such as instant tea granules or liquid ginseng extracts (pastes) are first dissolved in hot water, then passed through a Sep-Pak cartridge, following the procedure for ginseng root above.

The HPLC system utilized includes a Macherey-Nagel Nucleosil C18 column (100 X 4 mm, 120 Å pore, 5 μ particle, Dychrom, Santa Clara, CA). A gradient mobile phase with solvent A of 12% acetonitrile (J.T. Baker HPLC grade, VWR Scientific Products, San Francisco, CA) in water and solvent B of 100% acetonitrile was used. The gradient is increased linearly from 10 to 65% of solvent B over a period of 65 minutes. Detection is through a Shimadzu SPD-M6A photodiode array detector (Shimadzu Scientific Instrument, Columbia, MD) set at an analytical wavelength of 205nm. The injection volume is 40 microliters.

DISCUSSION

All ginseng roots or products evaluated were from the cultivated varieties. This study focused on the eight ginsenosides- R_{g1} , R_e , R_f , R_{g2} , R_{b1} , R_c , R_{b2} , and R_d - as identified by Schulten and Soldati⁴ (Figure 4). Analysis of some 18 samples of Asian ginseng and 8 samples of North American ginseng root found ginsenoside R_f , $C_{42}H_{72}O_{14}$, to be absent from the North American ginseng. The predominant components of North American ginseng are ginsenosides R_{b1} , $C_{54}H_{92}O_{23}$, and R_e , $C_{48}H_{82}O_{18}$. The North American root contains relatively low levels of R_{g1} , $C_{42}H_{72}O_{14}$, and R_{b2} , $C_{52}H_{90}O_{22}$. The Asian ginseng root however, contains ginsenoside R_f , as well as detectable levels of ginsenosides R_e , R_{g2} , R_{b1} , R_c , R_{b2} , R_d , and higher levels of R_{g1} . A similar pattern is observed in instant ginseng tea granules (Figure 5).

North American root cultivated in Vancouver, British Columbia was identical to root grown in Wisconsin. Preliminary studies show a difference between "Korean" red ginseng and the Chinese white ginseng. However, the "Korean" samples analyzed were not authenticated. Further studies are necessary to determine the geoclimatic significance and the impact that soil fertility and processing have on ginsenoside profiles.

While the North American and Asian ginsengs have almost opposite effects, both contain ginsenoside R_{b1} as the major saponin. Additionally, both varieties contain seven

common ginsenosides, though at different levels. The broad therapeutic value of ginseng is believed to be derived from this complex mixture of biologically active components, and not from any single compound.

CONCLUSION

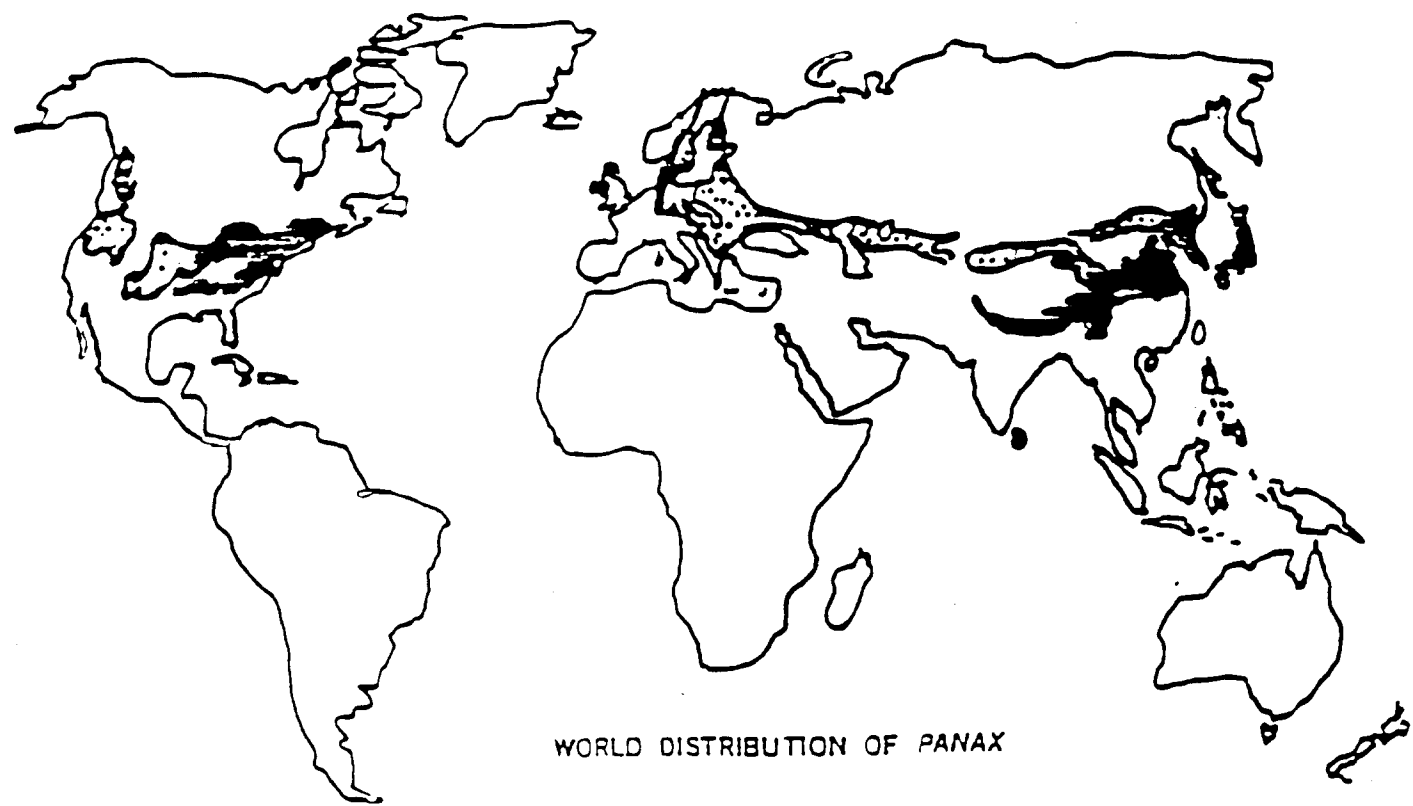
Ginseng is a widely used Asian herb. The North American ginseng is botanically different from the Asian ginseng. The two varieties have almost opposite therapeutic effects and command a different price in the marketplace. Examination of the ginsenoside profiles by HPLC allows us to authenticate the cultivated North American and Asian ginsengs.

ACKNOWLEDGMENTS

The author acknowledges Dr. Ron Rambadt of the Wisconsin Ginseng Board and Dr. Eric Littlely of Chai-Na-Tai Ginseng Products in Vancouver, B.C. for their insights and assistance in providing authentic references of ginseng root.

REFERENCES

1. Huang, Kee Chang, The Pharmacology of Chinese Herbs, CRC Press, Boca Raton, FL, 1993, pp21-45.
2. Hu, Shiu Ying, "The Ecology, Phytogeography and Ethnobotany of Ginseng" The Arnold Arboretum of Harvard University.
3. Cheung, Ka-Shing et. al., "Pharmacognostical Identification of American and Oriental Ginseng Roots by Genomic Fingerprinting Using Arbitrarily Primed Polymerase Chain Reaction (AP-PCR)", Journal of Ethnopharmacology, 42, 67-69, 1994, Elsevier Science Ireland, Ltd.
4. Schulten, H.R. and Soldati, F., "Identification of Ginsenosides from Panax Ginseng in Fractions Obtained by High-Performance Liquid Chromatography by Field Desorption Mass Spectrometry, Multiple Internal Reflection Infrared Spectroscopy and Thin-Layer Chromatography", Journal of Chromatography, 212, 37-49, 1981, Elsevier Scientific Publishing Company, Amsterdam.



WORLD DISTRIBUTION OF PANAX

Figure 1: World distribution of Ginseng. The darkened areas are where ginseng is known to exist. The dotted areas do not have high concentrations of ginseng. These areas have the winter chill but appear to lack the annual rainfall. The concentration of ginseng in the northern hemisphere of *eastern* North America and *eastern* Asia suggests a close floristic relationship of the eastern sides of the two continental masses³.

Ginsenoside Structure

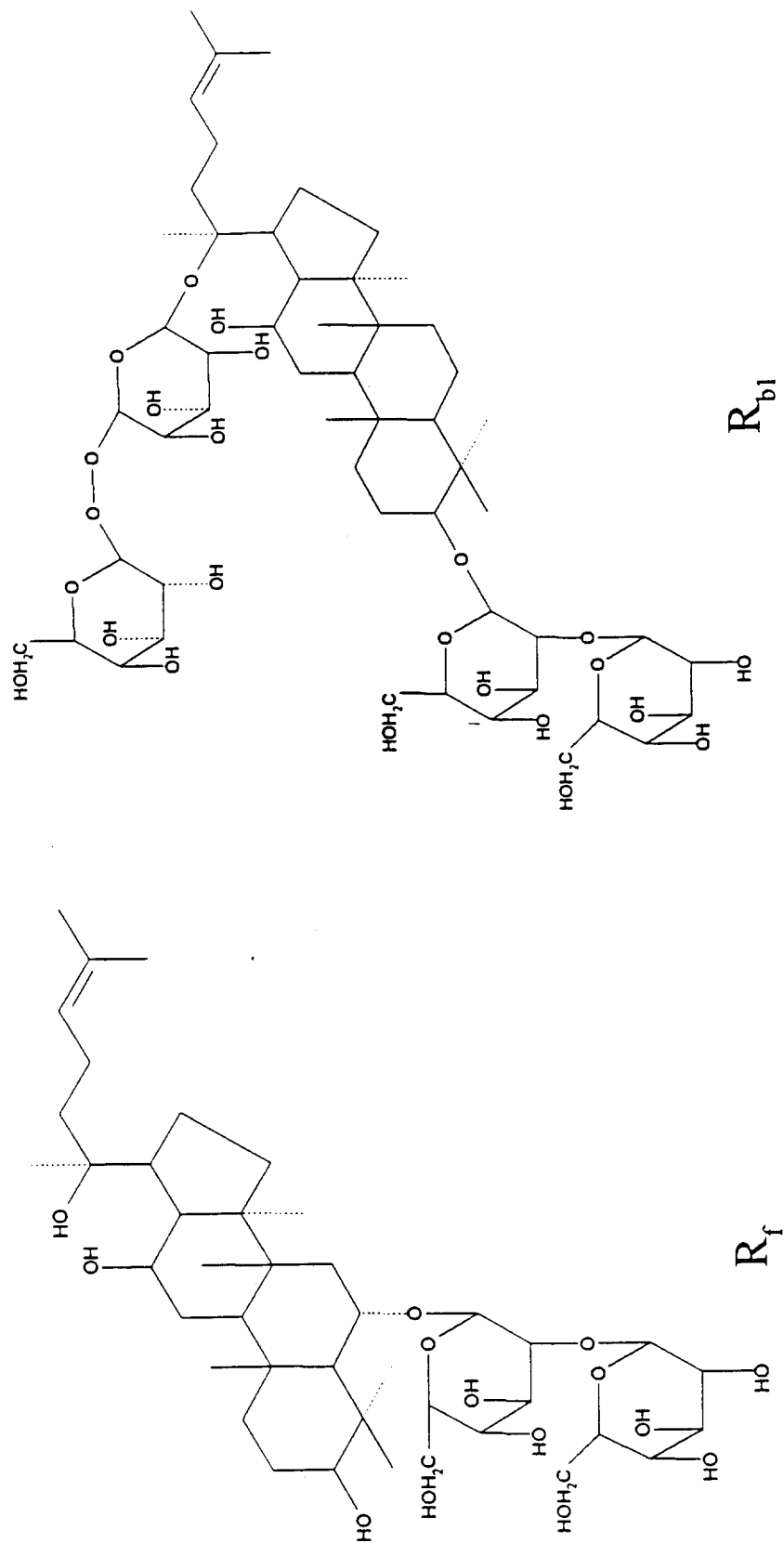


Figure 2. Structures of ginsenosides R_f , $C_{42}H_{72}O_{14}$ and R_{b1} , $C_{54}H_{92}O_{23}$. Ginsenosides are tetracyclic saponins.

Ginsenoside

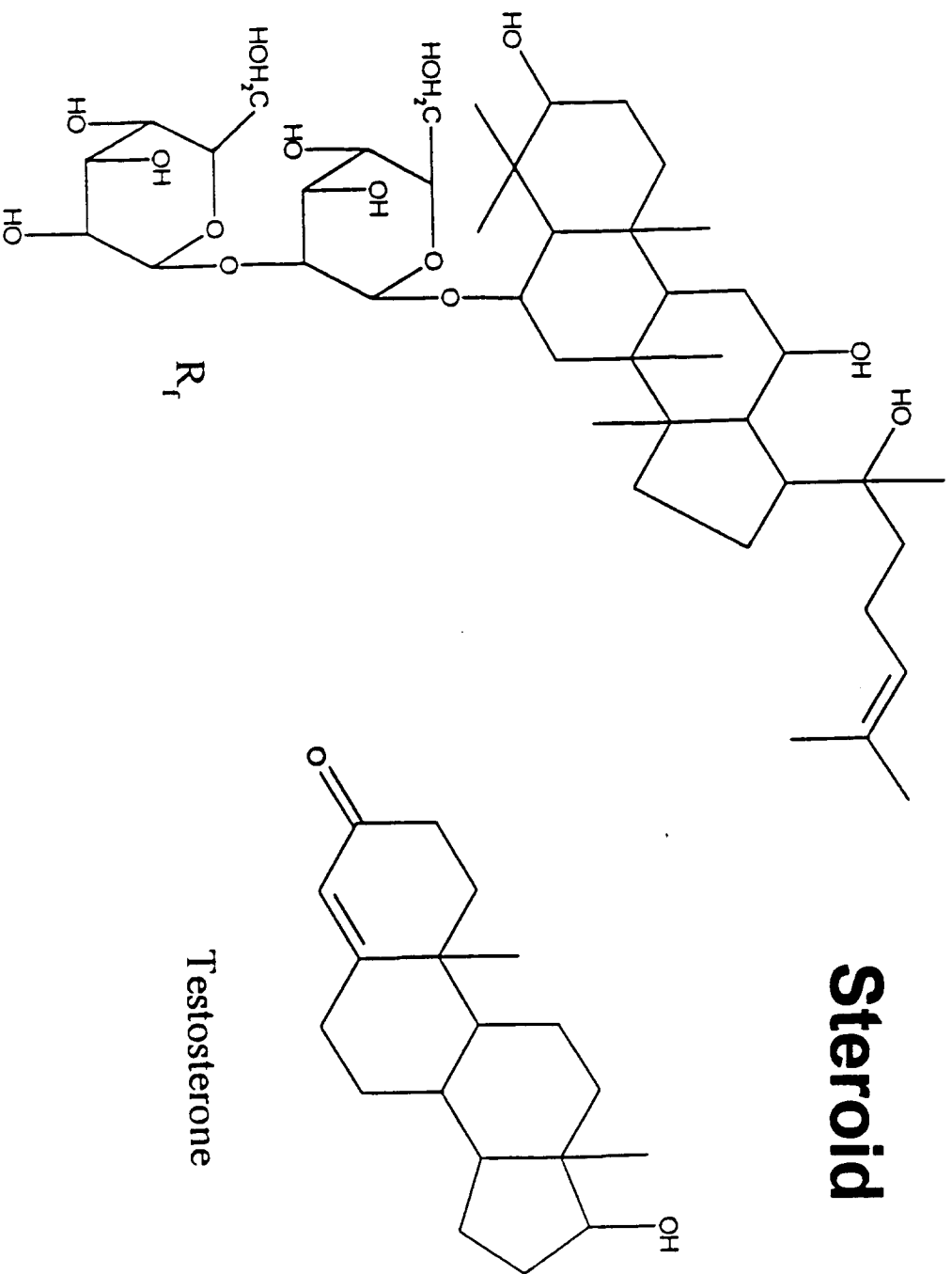


Figure 3: Structural similarity of ginsenosides and the sex hormone testosterone. Hydrolysis of the glycosidic ginsenoside R_1 yields a tetracyclic sapogenin structurally reminiscent of testosterone.

Ginseng Root

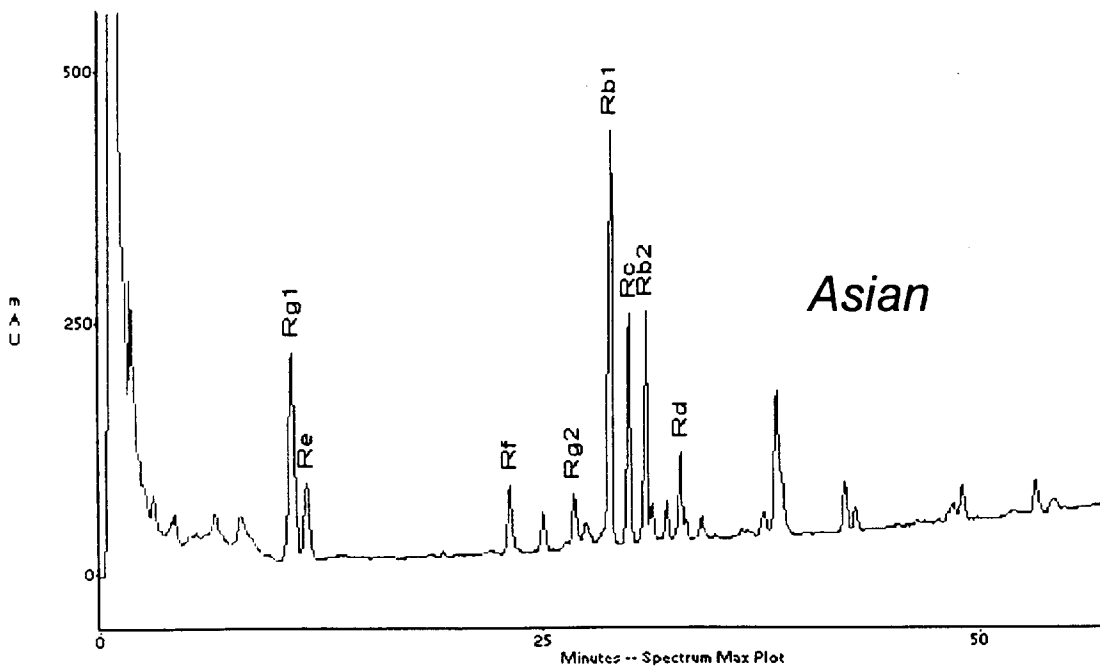
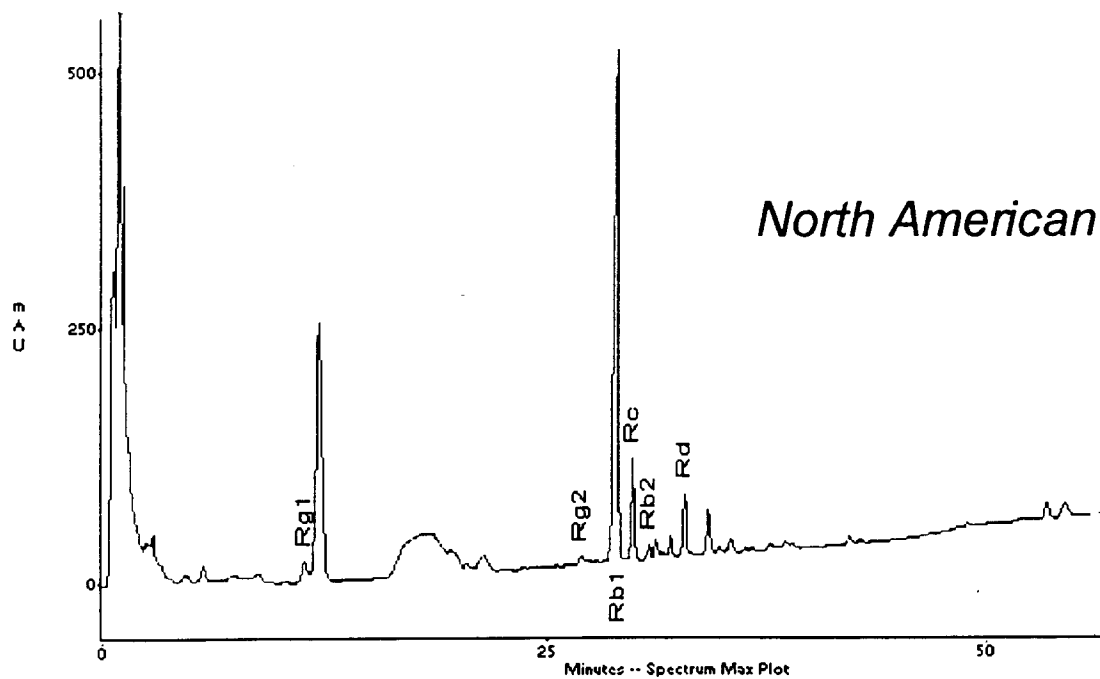


Figure 4: Ginsenoside profiles of North American (top) and Asian ginseng root. Note the absence of Rf in the North American root extract. Ginsenosides Rg1, Rb2, and Rb3 are present at higher levels in the Asian root extract.

Ginseng Teas

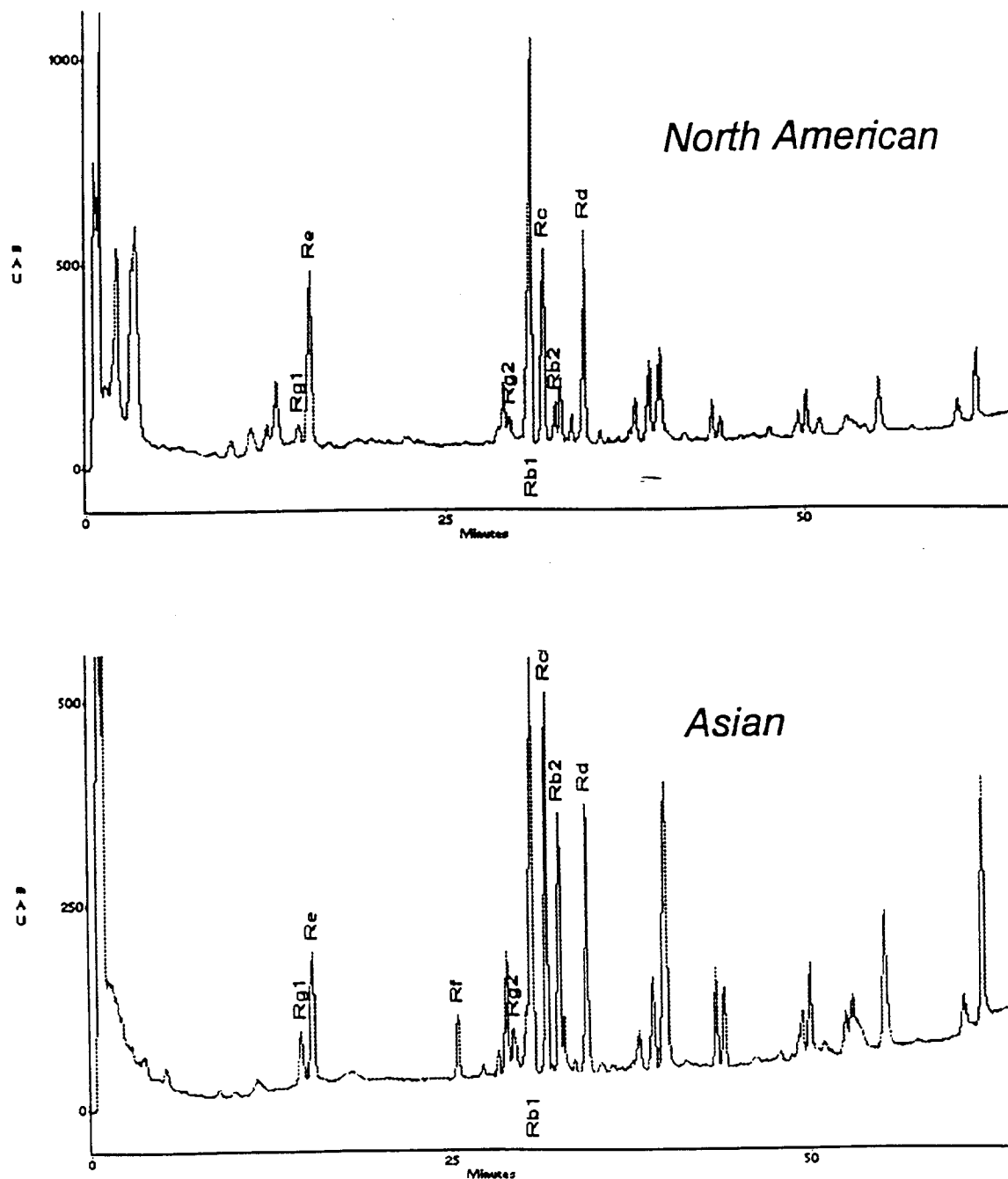


Figure 5: Ginsenoside profiles of North American and Asian instant ginseng tea granules. Ginsenoside R_f is absent from the North American product. The Asian instant tea contains higher levels of ginsenosides R_{g1} , R_c , and R_{b2} . The profile of the processed product is similar to the ginseng root.

FOOTWEAR IMPRESSION COMPARATIVE ANALYSIS BY COMPUTER IMAGING

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INTRODUCTION

The Los Angeles Customs Laboratory was requested by the Office of Investigations to perform a comparative analysis on photos of footwear impressions obtained at a desert site where 475 pounds of cocaine were allegedly dropped. A suspect was apprehended near the drop site. Through the use of computer imaging techniques, the laboratory was able to establish that one of the footwear impressions was the same size and design as the impression taken from the suspect's boots, and that a second impression was the same design. The laboratory's findings very likely contributed to the suspect pleading guilty.

EXPERIMENTAL

Computer Imaging Equipment and Software

- 1) Corel Draw 5.0 Graphic Suite software
- 2) Pentium 133 computer with Windows 3.1
- 3) Sony CCD color camera with zoom lens
- 4) Snappy image capture device
- 5) Hewlett-Packard flat bed scanner
- 6) Canon BJC 620 color printer

Samples Received

- 1) A color photograph of a footwear impression and a ruler on what appears to be sand. The outline of the entire sole impression is visible, but only the heel design is discernible.

- 2) A black and white photograph of a footwear impression on what appears to be sand. The partial design of the front sole is discernible but the heel design is barely visible. No ruler is included in the photograph.
- 3) A pair of black laced work boots worn by the suspect when he was arrested.

Sole Impression Comparison Methodology

Note: "Sample" refers to the footwear impression from the submitted photographs. "Reference" refers to the footwear impression made with the submitted boots.

- 1) Digital images of the sample photographs were taken using the flatbed scanner (See Images 1 and 2).
- 2) Impressions of the sole of the submitted right boot were obtained on a bed of sand purchased by the laboratory.
- 3) Digital images of the sand impressions were taken using the computer imaging system (See Images 3 through 6).

The following steps refer to the processing of the footwear impression from the first sample impression (Image 1):

- 1) The sample and reference images were rotated to have their long axis in horizontal position. Note: The software allows the rotation of the image in any specified angle.
- 2) The ruler in each of the sample and reference images was moved closer to the sample and rotated to be in line with the horizontal axis of the images.
- 3) The number of pixels representing a 3-inch length as it appears in the ruler in both the reference and sample images was determined. Note: The software displays the x and y coordinates of a cross-hair cursor which can be positioned at any location in the image. The difference between the two

x coordinates representing the 3-inch length is the number of pixels between the two points.

- 4) Based on the ratio of the number of pixels obtained, one image was adjusted to match the magnification of the other (See Images 7, 8, 10 and 11). Note: The software allows for the resizing of the image at any given percentage.
- 5) The sample and reference images were compared by taking a half section of the sole design from one of the images and superimposing it on the other image (See Images 9, 12 and 13). Note: The sand at the toe end of the outline of the entire sole impression (See Image 9) appears to have caved in (basis: it appears that the toe end is not consistent with the curvature of the front sole impression.) which may explain the slight difference in length when compared with the reference impression.

The following steps refer to the processing of the front sole impression from the second sample impression (Image 2):

- 1) Since there is no ruler included in the sample photograph, magnification adjustment was based on the ratio of the measured lengths of the wedge design in the sole of the sample and reference (See Image 14 and 15).
- 2) The images were compared in the same fashion as the first sample impressions (See Image 16).

RESULTS AND DISCUSSION

As can be seen from the superimposition of the sample and reference images (See Images 9, 12, 13 and 16), the sample sole impression in Image 1 is of the same size and design as the sole impression from the submitted right boot, and the sole impression in Image 2 is of the same design. NOTE: "The same size" cannot be concluded in Image 2 since there is no ruler included in the sample photograph.

The soles of the submitted boots are injection molded and do not show any design characteristics, imperfections or damages which can be uniquely identified with the sole impression found at the cocaine drop site.

The image capture device (Snappy) used in the analysis is a very good and inexpensive (approximately \$199) alternative to other frame grabbers costing several thousand dollars. The device can capture at a higher resolution (1500 X 1125 pixels) than some expensive frame grabbers on the market.

The software (Corel Draw graphic suite) used in the analysis is well suited for the manipulation of images involving enhancement, rotation, resizing, cropping and superimposition of images. The software is also well suited for making presentation exhibits for courtroom purposes.

CONCLUSION

This work showed that consumer software and devices like Corel Draw, HP ScanJet and Snappy intended for the general public are more than adequate for some image comparative analysis. They are usually easier to use and do not require specialized training compared to scientific-oriented software and devices.

SCANNED IMAGES OF SUBMITTED PHOTOGRAPHS
(SAMPLE IMPRESSIONS)

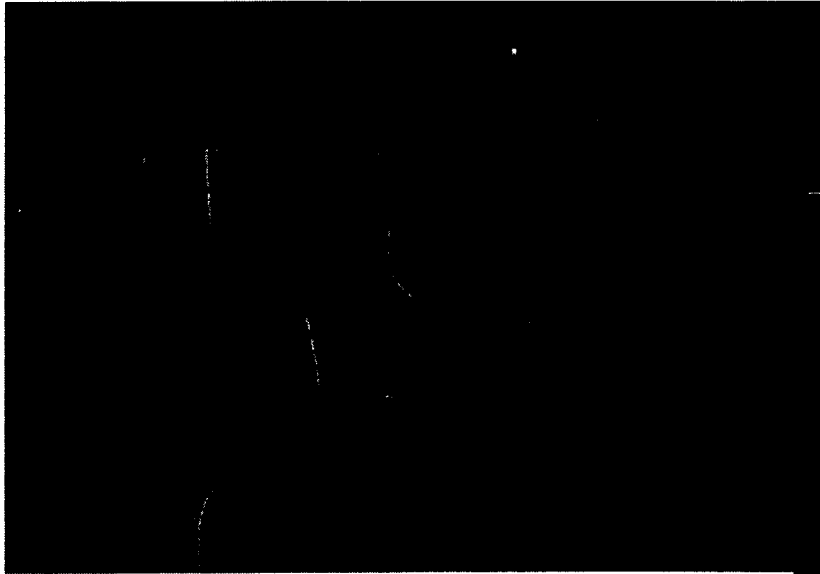


Image 1. First footwear impression obtained at the cocaine drop site



Image 2. Second footwear impression obtained at the cocaine drop site

REFERENCE IMPRESSIONS

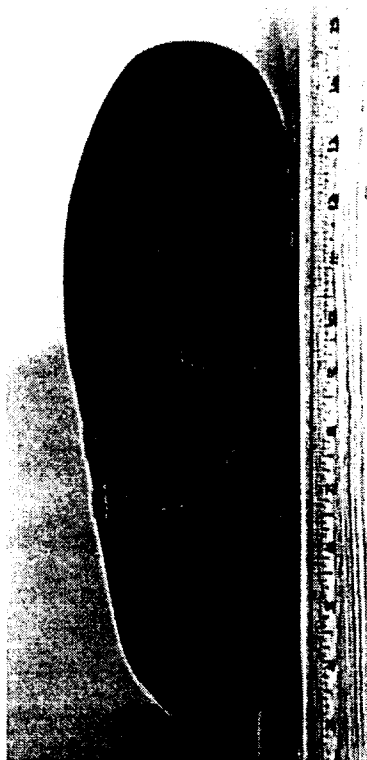


Image 3. Sole of submitted boot

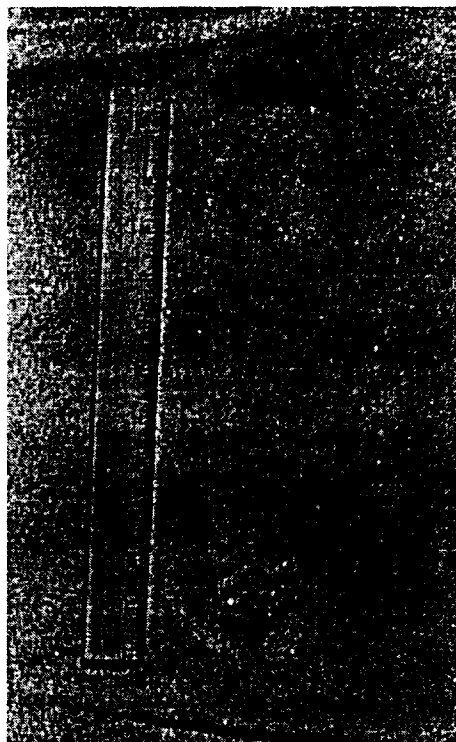


Image 4. Sand impression of the entire sole

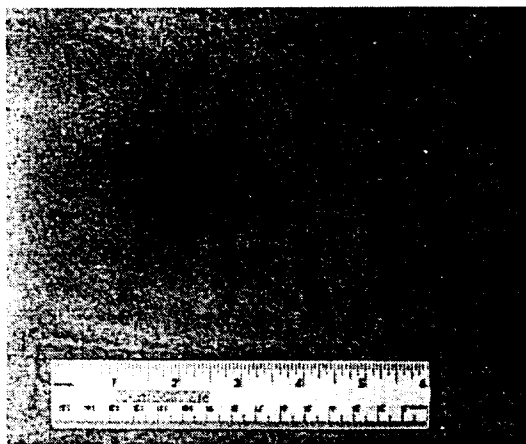


Image 5. Sand impression of the front sole

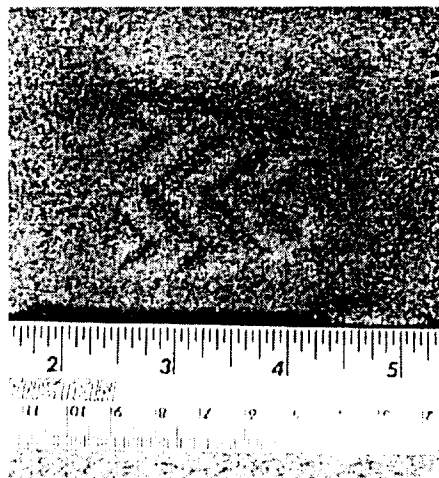


Image 6. Sand impression of the heel

ENTIRE SOLE COMPARISON

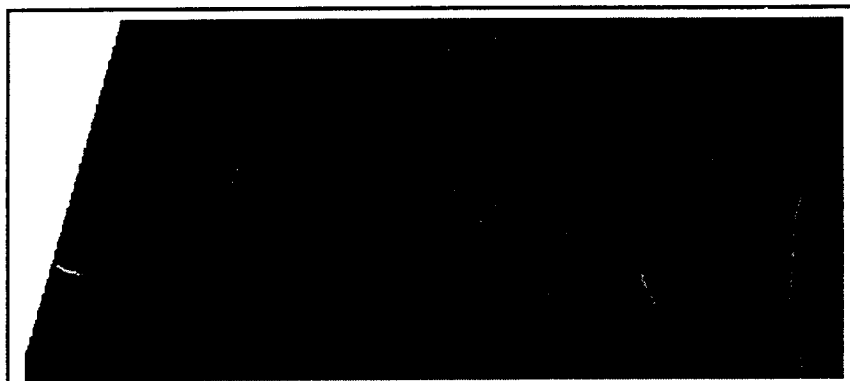


Image 7. Sample impression.

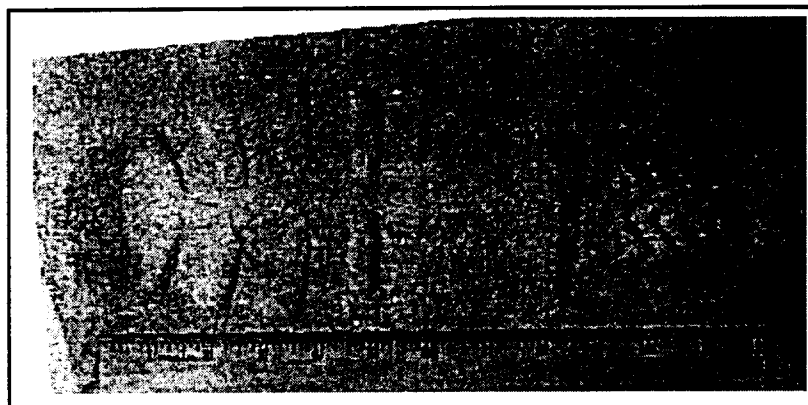


Image 8. Reference impression.

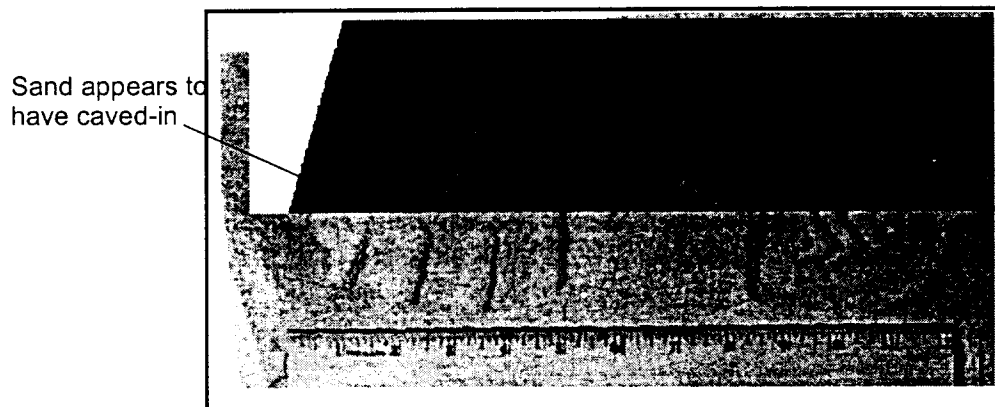


Image 9. Half section of the sample impression superimposed on the reference impression.

HEEL IMPRESSION COMPARISON

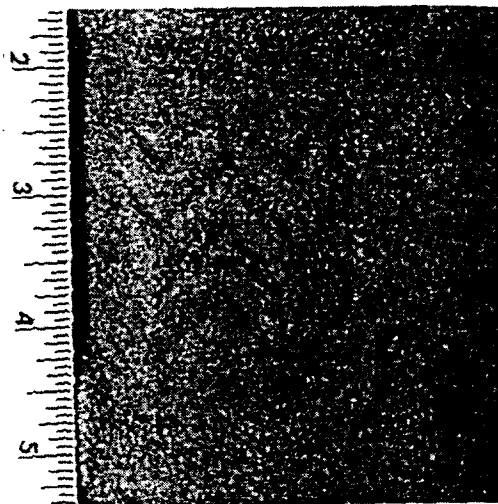


Image 10. Reference impression



Image 11. Sample impression

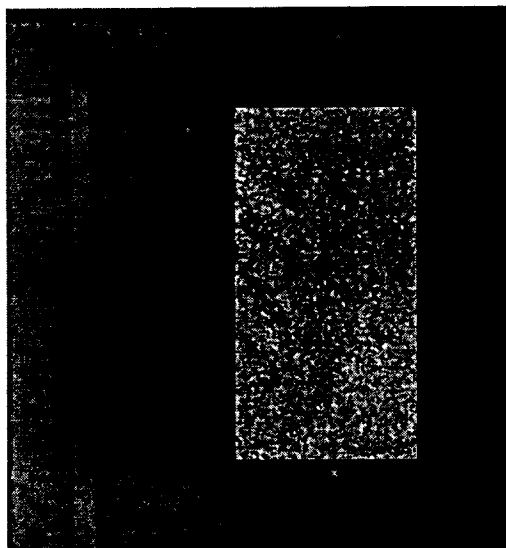


Image 12. Right half section of the reference impression superimposed on the sample impression

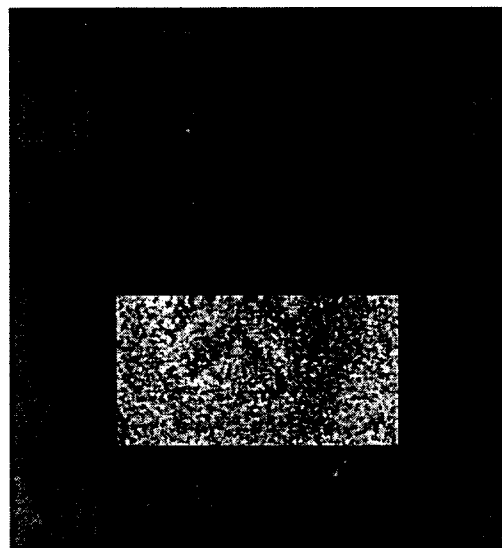


Image 13. Bottom half section of the reference impression superimposed on the sample impression

FRONT SOLE COMPARISON

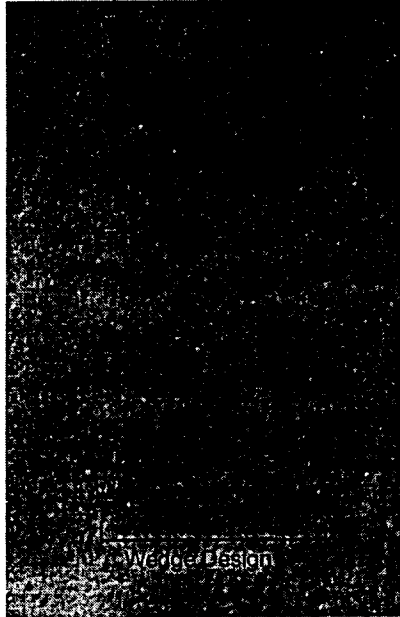


Image 14. Reference impression



Image 15. Sample impression



Image 16. Right half section of the sample impression superimposed on the reference impression

“BURN-OUT” WOVEN FABRIC

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U.S. Customs Laboratory, Los Angeles, CA

INTRODUCTION

Burn-out (or burnt-out) fabric is defined as “a fabric or lace made with two different yarns with a pattern effect produced by destroying one of the yarns in a printing process that employs chemicals instead of color.” [1]

Fabrics composed of yarns of different colors, containing plain woven background portions and repeating “burn out” floral designs, have been received in the laboratory (See Figure 1). The perimeters of these “burn-out” areas are usually printed with coloring matter to complete the floral effect. Also, fabrics have been received in the laboratory exhibiting the reverse, that is, the repeating floral designs are woven and printed, and the backgrounds contain “burn-out” areas (See Figure 2).

The Harmonized Tariff Schedule of the United States (HTSUS), Section XI has many areas where weave determination is necessary for classification. Specifically, fabrics could be entered with HTSUS heading 5407.94.20.20, which is the classification for plain woven and printed woven fabrics of synthetic filament yarn. [2] The competing provision, 5407.94.20.90, is for printed fabric of synthetic filaments containing other than plain, satin, or twill woven construction. The difference in these two classifications is a difference in required visa. The question asked by Import Specialists is, “What is the weave type?”

EXPERIMENTAL

The fabric is conditioned per HTSUS, Section XI, General Explanatory Note (IV), “Standard Atmospheres For Conditioning and Testing of Textiles.”

The fabric is examined using an Olympus Model SZH stereo microscope at a magnification of 10x. In particular, the “burn-out” areas are studied intensively. The yarns in these areas are examined for partially dissolved ends. A partially dissolved yarn has a melted or frayed and cut appearance at the end of the yarn. All observations are recorded.

The “burn-out” areas and adjacent areas forming a pattern repeat are plotted per standard basic weave type determination procedures (as referenced in HTSUS, Section XI, General Explanatory Notes (I)(C), Subheading Explanatory Notes, and as described in ASTM D579, section 33). [2] [3]

RESULTS AND DISCUSSION

The fabric exhibits a plain woven construction (1 x 1 interlacing) in some areas and not in others. These other “open appearance” areas consist of an absence of yarn, such as rayon in this case, which has been “dissolved” in order to achieve a specialized “motif appearance.” Refer to Figure 1.

The definition of a plain woven fabric per HTSUS, Section XI, Subheading Note 1(k) is “a fabric construction in which each yarn of the weft passes alternately over and under successive yarns of the warp and each yarn of the warp passes alternately over and under successive yarns of the weft.” This does not occur in those “open appearance” areas since there are no successive yarns and there is no interlacing effect.

HTSUS, Chapter 54, Statistical Note 1 (a) states “for the purposes of woven fabrics of Chapter 54: (a) Unless the context otherwise requires, provisions relating to one or more weaves embrace only those fabrics which (excluding selvage) are wholly of the specified weave or weaves, including combinations exclusively thereof.”

The term “wholly of” is also defined in HTSUS, General Notes 19(e)(i) as “...means that the goods are, except for negligible or insignificant quantities of some other material or materials”, composed completely of the named material...”

A “burn-out” fabric is not wholly of plain weave. There is an issue that the “open appearance” effect is not produced on the loom and therefore could conceivably still be considered plain woven. We as Customs scientists are obligated to address such issues and report results relating to HTSUS, applicable HTSUS notes, rulings, and available reference literature.

Referring back to the definition of plain weave in the HTSUS, plain weave is a construction. It is not defined that if the fabric has a plain woven construction directly off the loom, it will always be considered plain woven. According to HTSUS, Additional U.S. Rules of Interpretation 1(a), “a tariff classification controlled by use (other than actual use) is to be determined in accordance with the use in the United States at, or immediately prior to, the date of importation, of goods of that class or kind to which the imported goods belong, and the controlling use is the principal use...”

Also, there are numerous examples in the tariff that exhibit classification based on further processing of plain woven loom state goods. Some of these examples are embroidered fabric, applique work, and quilted fabric in HTSUS, Section XI, Explanatory Notes 58.10 and 58.11. Also, many processes change the final classification of loom state goods, such as dyeing, printing in HTSUS, Section XI Explanatory Notes, Subheading Note 1, or laminating with plastic as per HTSUS, Chapter 59, Note 2. Even yarns after they are produced and are further processed (metallized, gimped, or loop wale as in HTSUS, Section XI, Explanatory Notes 56.05 and 56.06), change classification.

CONCLUSION

The “burn-out” fabric exhibits two types of constructions. The woven background portion has a plain woven construction. The floral design portion contains warp yarns and weft yarns, some of which have been dissolved leaving an “open” area which is other than plain, duck, satin, or twill construction. (The reverse pattern—plain woven floral design and “open” area background—also exhibits two types of constructions.) These samples have the characteristics of “other” woven constructions. An example of a laboratory report narrative follows:

“The sample exhibits two types of constructions. The woven background portion has a plain woven construction. The floral design portion contains warp yarns and weft yarns, some of which have been dissolved leaving an “open motif which is other than plain, duck, satin, twill, or oxford construction.”

REFERENCES

1. Wingate, Isabel, "Fairchild's Dictionary of Textiles," Fairchild Publications, New York, 1984.
2. Harmonized Tariff Schedule of the United States, Annotated (1997) and Explanatory Notes.
3. Annual Book of ASTM Standards, Volume 7.01, 1986.



Figure 1. "Burn-out" floral motif

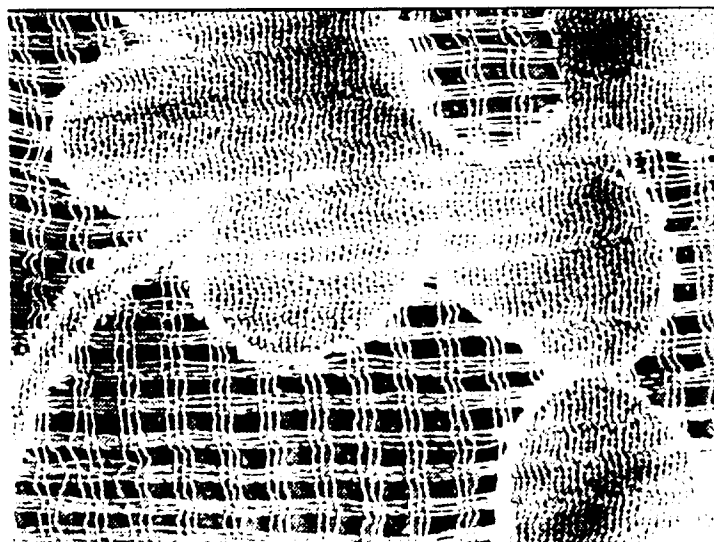


Figure 2. "Burn-out" background

**SUGAR ANALYSIS -
A COMPARATIVE STUDY BETWEEN THE
ICUMSA METHOD AND THE NEAR INFRARED
SPECTROSCOPY METHOD**

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INTRODUCTION

The U.S. Customs Laboratory system has an interest in eliminating the use of lead subacetate from our sugar analyses procedure. Currently, most U.S. sugar refinery laboratories are using the NIR (near infrared) non-lead method that measures the optical rotation of sugar solutions at 880 NM. The reason these laboratories are using the non-lead method is simply to eliminate a toxic waste. Additional U.S. Note 1 to Chapter 17, HTSUSA (Harmonized Tariff Schedule of the United States) states, "The term 'degree' as used in the 'Rates of Duty' columns of this chapter means International Sugar Degree as determined by polarimetric test performed in accordance with procedures recognized by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA)" (1). The recognized ICUMSA method is the polarimetric spectroscopy (lead) method that measures the optical rotation of sugar solutions at approximately 589nm (2). In this study, we compare the NIR (non-lead) method and the ICUMSA (lead) method to investigate the impact on duty and quota quantities that would result from adopting the NIR method.

The amount of duty collected and quantities of sugar allowed into the country depend on the average polarization in degree α determined analytically. If the average polarization between the methods is the same then use of the NIR method would be revenue and quota neutral. In this study we determined that the methods are essentially revenue and quota neutral, however some differences were observed.

EXPERIMENTAL

Sugar samples from 14 entries representing seven countries received over the past year were analyzed by both methods. The lead method was performed using an AUTOPOL III automatic polarimeter (Rudolph Research, Fairfield, N.J.) following the ICUMSA method (2). The near infrared spectroscopy (non-lead) method was performed using a Polartronic NIR spectrometer (Schmidt and Haensch, Naumannstraße, Berlin) following the method outlined in United States National Committee on Sugar Analysis (USNC) Proceedings, 1993 Meeting (3).

RESULTS AND DISCUSSION

We have found the sugar polarization values obtained from both methods very similar for most entries. We subtracted 'the average NIR (non-lead) reading' from 'the average ICUMSA (lead) reading' for each entry (see Figure 1 and Table 1) and determined the total average difference for all these entries to be -0.02 (degree z). The average weighed difference is also determined. The average weighed difference is the average difference of each entry multiplied by the number of samples that produced the average difference added then divided by the total number of samples for all the entries. This measurement weighs all samples equally. The average weighed difference for all the data was -0.02 (degree z). This result indicates the methods are essentially revenue and quota neutral. The complete set of data is listed in Appendix I.

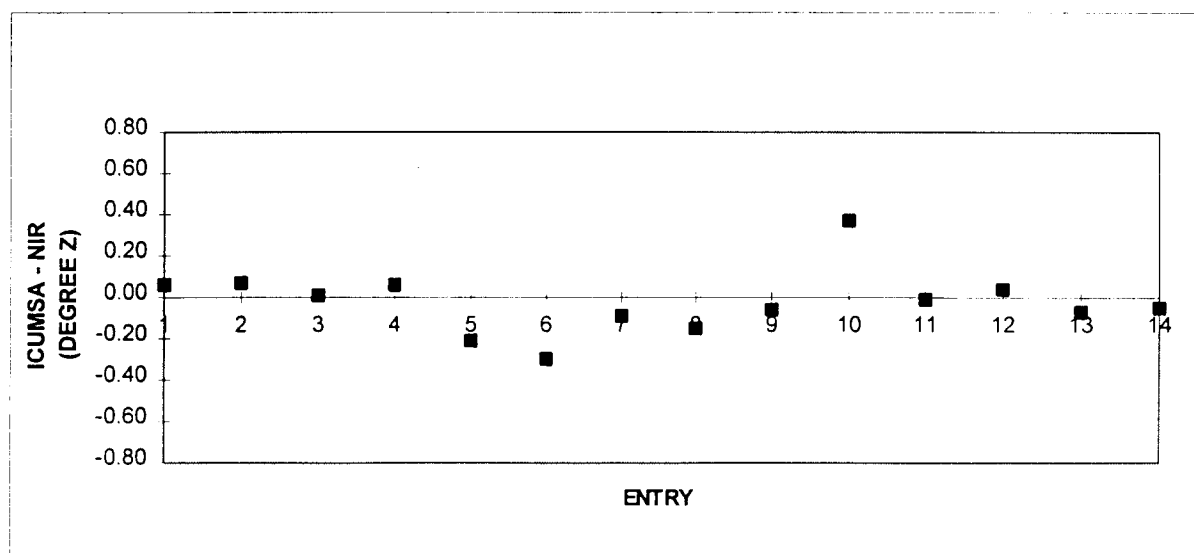


Figure 1. The Average Difference ICUMSA - NIR (in degree z)

TABLE 1. Sugar Analysis ICUMSA vs. NIR Method

ID NUMBER	COUNTRY	AVERAGE DIFFERENCE (degree z)	NUMBER OF SAMPLES	WEIGHED DIFFERENCE (degree z)
1	BRAZIL	0.06	22	1.32
2	BRAZIL	0.07	28	1.96
3	BRAZIL	0.01	26	0.26
4	COLOMBIA	0.06	10	0.60
5	COLOMBIA	-0.21	3	-0.63
6	DOMINICAN	-0.30	11	-3.30
7	DOMINICAN	-0.09	16	-1.44
8	GUATEMALA	-0.15	28	-4.20
9	GUATEMALA	-0.06	16	-0.96
10	HONDURAS	0.37	9	3.33
11	HONDURAS	-0.01	8	-0.08
12	MEXICO	0.04	15	0.60
13	NICARAGUA	-0.07	15	-1.05
14	NICARAGUA	-0.05	22	-1.10
	AVERAGE	-0.02		-0.02
	TOTAL		229	

Using the guidelines of the A.O.A.C. manual Use of Statistics to Develop and Evaluate Analytical Methods (4) a statistical method called ANOVA (Analysis of Variance), shows that four of the 14 entries (See Figure 2 and Table 2) had Fisher values that were greater than the expected F-critical value. This result indicates there are some unknown differences between the two analytical methods under investigation. These findings are consistent with the experimental results of other studies (5) and are attributed to the influence of non-sugars on the optical rotation of light at differing wavelengths (6).

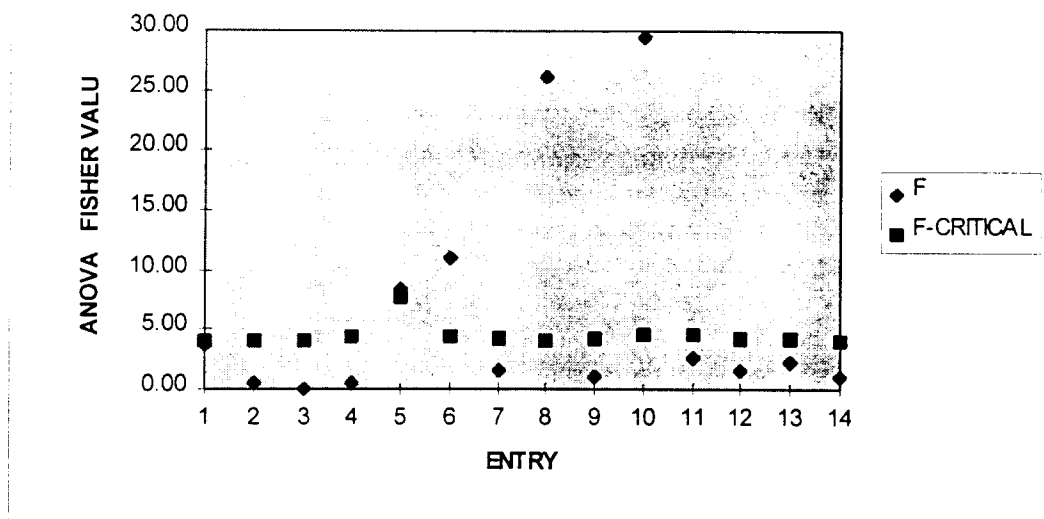


Figure 2. F vs. F-Critical Values For 14 Sugar Entries

TABLE 2. FISHER VALUES FOR ANALYSIS OF VARIANCE

ID NUMBER	COUNTRY	NUMBER OF SAMPLES	F	F-CRITICAL
1	BRAZIL	22	3.75	4.07
2	BRAZIL	28	0.44	4.02
3	BRAZIL	26	0.04	4.03
4	COLOMBIA	10	0.55	4.41
5	COLOMBIA	3	8.34	7.71
6	DOMINICAN	11	10.91	4.35
7	DOMINICAN	16	1.55	4.17
8	GUATEMALA	28	26.18	4.02
9	GUATEMALA	16	1.06	4.17
10	HONDURAS	9	29.48	4.49
11	HONDURAS	8	2.69	4.60
12	MEXICO	15	1.63	4.20
13	NICARAGUA	15	2.32	4.20
14	NICARAGUA	22	1.11	4.07

CONCLUSIONS

'The Average Difference Analysis' and 'Average Weighed Difference Analysis' demonstrates that both methods produce essentially the same average polarization values. This is consistent with the data reported by the New York Sugar Trade Laboratory Study (SIT PAPER # 677, Statistics of Raw Sugar Settlement Polarizations Non lead vs. Lead Method). (5) The differences between the methods appear to be too small to impact revenue collection or quantities for quota purposes.

REFERENCES

1. Harmonized Tariff Schedule of the United States (1997), Additional U.S. Notes 1, Chapter 17, United States International Trade Commission, Washington D.C..
2. Method GS1/2/3-1 (1994) The Determination of the Polarisation of Raw Sugar by Polarimetry.
3. Proceedings of the United States National Committee on Sugar Analysis, 1993 Meeting, Report on General Subject GS-1, Raw Sugar, Walter Altenberg, Referee. Copies can be obtained from Mary An Godshall 1100 Robert E. Lee Blvd., New Orleans, LA 70124 Telephone (504) 282-5387.
4. Wernimont, Grant, Use of Statistics to Develop and Evaluate Analytical Methods, A.O.A.C. International, Arlington, VA, p.28, 1985.
5. Altenburg, Walter, Margaret, Nemeth, and Chou, Chung, Statistics of Raw Sugar Settlement Polarizations Non-Lead vs. Lead Method, SIT PAPER # 677, Sugar Industry Technologist, May 1995 meeting.
6. Chen, James C.P., International Sugar Journal, 1993, 95

APPENDIX I

IDENTIFICATION NUMBER: 1
COUNTRY OF ORIGIN: BRAZIL

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.51	98.35	0.16
2	98.56	98.51	0.05
3	98.51	98.52	-0.01
4	98.40	98.33	0.07
5	98.44	98.47	-0.03
6	98.48	98.51	-0.03
7	98.54	98.43	0.11
8	98.59	98.46	0.13
9	98.42	98.33	0.09
10	98.48	98.43	0.05
11	98.66	98.18	0.48
12	98.40	98.32	0.08
13	98.57	98.40	0.17
14	98.25	98.34	-0.09
15	98.48	98.33	0.15
16	98.41	98.23	0.18
17	98.47	98.30	0.17
18	98.40	98.28	0.12
19	98.47	98.53	-0.06
20	98.45	98.54	-0.09
21	98.23	98.35	-0.12
22	98.28	98.51	-0.23
	Average Difference (degree z)		0.06

IDENTIFICATION NUMBER: 2
COUNTRY OF ORIGIN: BRAZIL

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.83	98.61	0.22
2	98.86	98.63	0.23
3	98.89	98.84	0.05
4	99.02	98.97	0.05
5	98.77	98.90	-0.13
6	99.04	98.87	0.17
7	99.03	98.94	0.09
8	98.96	98.87	0.09
9	98.82	98.98	-0.16
10	99.06	98.77	0.29
11	99.05	98.80	0.25
12	99.00	98.85	0.15
13	98.80	98.88	-0.08
14	98.95	98.56	0.39
15	98.42	98.51	-0.09
16	98.66	99.24	-0.58
17	98.64	98.71	-0.07
18	98.30	98.42	-0.12
19	98.25	98.47	-0.22
20	98.19	96.42	1.77
21	98.32	98.39	-0.07
22	98.78	99.02	-0.24
23	98.84	98.87	-0.03
24	98.95	98.90	0.05
25	98.58	98.70	-0.12
26	98.69	98.59	0.10
27	98.69	98.77	-0.08
28	98.64	98.63	0.01
	Average Difference (degree z)		0.07

IDENTIFICATION NUMBER: 3
COUNTRY OF ORIGIN: BRAZIL

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.69	98.52	0.17
2	98.93	98.63	0.30
3	98.66	98.52	0.14
4	98.94	98.79	0.15
5	98.95	98.70	0.25
6	98.66	98.53	0.13
7	98.83	98.87	-0.04
8	98.51	98.49	0.02
9	98.54	98.52	0.02
10	98.92	98.74	0.18
11	98.88	98.66	0.22
12	98.86	98.75	0.11
13	98.81	98.45	0.36
14	99.12	99.09	0.03
15	98.91	99.09	-0.18
16	98.49	99.14	-0.65
17	98.65	98.87	-0.22
18	98.78	98.98	-0.20
19	98.34	98.55	-0.21
20	98.58	98.73	-0.15
21	98.69	98.86	-0.17
22	98.69	98.35	0.34
23	98.31	98.41	-0.10
24	98.34	98.44	-0.10
25	98.55	98.55	0.00
26	98.56	98.66	-0.10

Average Difference (degree z) 0.01

IDENTIFICATION NUMBER: 4
COUNTRY OF ORIGIN: COLOMBIA

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.32	98.24	0.08
2	98.23	98.23	0.00
3	98.23	98.28	-0.05
4	98.32	98.28	0.04
5	98.13	98.49	-0.36
6	98.20	98.25	-0.05
7	98.36	98.35	0.01
8	98.30	97.87	0.43
9	98.81	98.19	0.62
10	98.10	98.23	-0.13

Average Difference (degree z) 0.06

IDENTIFICATION NUMBER: 5
COUNTRY OF ORIGIN: COLOMBIA

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	99.02	99.10	-0.08
2	98.95	99.32	-0.37
3	98.95	99.13	-0.18

Average Difference (degree z) -0.21

IDENTIFICATION NUMBER: 6
COUNTRY OF ORIGIN: DOMINICAN REPUBLIC

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.95	99.70	-0.75
2	98.94	98.86	0.08
3	98.75	99.09	-0.34
4	98.98	99.18	-0.20
5	98.97	99.85	-0.88
6	98.87	99.24	-0.37
7	98.90	99.32	-0.42
8	98.93	99.08	-0.15
9	99.03	99.03	0.00
10	98.94	99.03	-0.09
11	98.96	99.18	-0.22
	Average Difference (degree z)		-0.30

IDENTIFICATION NUMBER: 7
COUNTRY OF ORIGIN: DOMINICAN REPUBLIC

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	97.66	97.16	0.50
2	97.67	97.80	-0.13
3	97.67	97.84	-0.17
4	97.54	97.64	-0.10
5	97.48	97.64	-0.16
6	97.63	97.58	0.05
7	97.68	97.58	0.10
8	97.69	97.69	0.00
9	97.55	97.50	0.05
10	97.48	97.60	-0.12
11	97.60	97.54	0.06
12	97.47	97.54	-0.07
13	97.55	97.36	0.19
14	97.28	97.52	-0.24
15	97.40	98.04	-0.64
16	97.53	98.22	-0.69
	Average Difference (degree z)		-0.09

IDENTIFICATION NUMBER: 8
COUNTRY OF ORIGIN: GUATEMALA

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	99.24	99.49	-0.25
2	99.14	99.30	-0.16
3	99.08	99.30	-0.22
4	99.15	99.33	-0.18
5	99.11	99.25	-0.14
6	99.28	99.49	-0.21
7	99.13	99.41	-0.28
8	99.20	99.40	-0.20
9	99.06	99.16	-0.10
10	99.18	99.36	-0.18
11	99.25	99.34	-0.09
12	99.08	99.23	-0.15
13	99.24	99.31	-0.07
14	99.14	99.29	-0.15
15	99.09	99.40	-0.31
16	99.06	99.16	-0.10
17	98.99	99.12	-0.13
18	99.03	99.12	-0.09
19	99.21	99.25	-0.04
20	99.01	98.92	0.09
21	99.25	99.29	-0.04
22	99.15	99.31	-0.16
23	99.15	99.41	-0.26
24	99.11	99.24	-0.13
25	99.31	99.26	0.05
26	99.18	99.34	-0.16
27	99.20	99.49	-0.29
28	99.19	99.30	-0.11
Average Difference (degree z)			-0.15

IDENTIFICATION NUMBER: 9
COUNTRY OF ORIGIN: GUATEMALA

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.68	98.49	0.19
2	98.69	98.63	0.06
3	98.68	98.71	-0.03
4	98.82	98.84	-0.02
5	98.65	98.82	-0.17
6	98.75	98.71	0.04
7	98.91	98.85	0.06
8	98.51	98.52	-0.01
9	98.67	98.72	-0.05
10	98.86	98.92	-0.06
11	98.59	98.71	-0.12
12	98.98	98.95	0.03
13	98.69	98.79	-0.10
14	98.78	98.89	-0.11
15	98.94	99.13	-0.19
16	98.75	99.24	-0.49
Average Difference (degree z)			-0.06

IDENTIFICATION NUMBER: 10
COUNTRY OF ORIGIN: HONDURAS

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.63	98.13	0.50
2	98.68	98.09	0.59
3	98.61	98.32	0.29
4	98.69	98.52	0.17
5	98.84	98.41	0.43
6	98.82	98.49	0.33
7	98.94	98.52	0.42
8	98.77	98.53	0.24
9	98.83	98.48	0.35
Average Difference (degree z)			0.37

IDENTIFICATION NUMBER: 11
COUNTRY OF ORIGIN: HONDURAS

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.20	98.23	-0.03
2	98.28	98.26	0.02
3	98.27	98.26	0.01
4	98.11	98.20	-0.09
5	98.10	98.17	-0.07
6	98.19	98.37	-0.18
7	98.08	98.22	-0.14
8	98.28	98.28	0.00
Average Difference (degree z)			-0.01

IDENTIFICATION NUMBER: 12
COUNTRY OF ORIGIN: MEXICO

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	98.51	98.34	0.17
2	98.57	98.51	0.06
3	98.56	98.45	0.11
4	98.63	98.45	0.18
5	98.53	98.47	0.06
6	98.45	98.50	-0.05
7	98.57	98.53	0.04
8	98.65	98.58	0.07
9	98.62	98.56	0.06
10	98.57	98.50	0.07
11	98.60	98.59	0.01
12	98.60	98.61	-0.01
13	98.60	98.45	0.15
14	98.66	98.62	0.04
15	98.54	98.86	-0.32
Average Difference (degree z)			0.04

IDENTIFICATION NUMBER: 13
COUNTRY OF ORIGIN: NICARAGUA

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	97.45	97.45	0.00
2	97.55	97.64	-0.09
3	97.69	97.83	-0.14
4	97.80	97.89	-0.09
5	97.55	97.59	-0.04
6	97.66	97.60	0.06
7	97.60	97.53	0.07
8	97.62	97.56	0.06
9	97.63	97.59	0.04
10	97.52	97.67	-0.15
11	97.50	97.44	0.06
12	97.65	97.77	-0.12
13	97.49	97.73	-0.24
14	97.49	97.59	-0.10
15	97.58	97.94	-0.36
	Average Difference (degree z)		-0.07

IDENTIFICATION NUMBER: 14
COUNTRY OF ORIGIN: NICARAGUA

	LEAD (degree z)	NIR (degree z)	DIFFERENCE (degree z)
1	97.62	97.49	0.13
2	97.30	97.51	-0.21
3	97.75	97.79	-0.04
4	97.47	97.48	-0.01
5	97.80	97.71	0.09
6	97.44	97.54	-0.10
7	97.76	97.82	-0.06
8	97.71	97.60	0.11
9	97.65	97.65	0.00
10	97.59	97.65	-0.06
11	97.72	97.61	0.11
12	97.65	97.68	-0.03
13	97.68	97.73	-0.05
14	97.73	98.01	-0.28
15	97.70	97.95	-0.25
16	97.77	98.13	-0.36
17	97.82	97.56	0.26
18	97.55	97.73	-0.18
19	97.50	97.60	-0.10
20	97.71	97.74	-0.03
21	97.66	97.71	-0.05
22	97.73	97.66	0.07
	Average Difference (degree z)		-0.05

**DETERMINATION OF ETHANOL AND WATER CONTENT IN ODORIFEROUS
SUBSTANCES BY CAPILLARY GAS CHROMATOGRAPHY**

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INTRODUCTION

The Harmonized Tariff Schedule of the United States (HTSUS) describes U.S. Customs regulations regarding odoriferous substances in Chapter 33. HTSUS heading 3301 deals with essential oils, 3302 with mixtures of odoriferous substances and 3303 with perfumes and toilet waters.

An essential oil is "a volatile oil derived from the leaves, stems, flowers or twigs of plants and usually carrying the odor and flavor of the plant" (1). Essential oils can also be derived from fruit, roots or wood from a wide variety of plants. Since the resultant fragrance is sensed by the olfactory organs as being the "essence" of the fragrance of that the particular plant, the essential oil, then, consists of pure "essence" without additional alcohols or water and may be composed of predominantly one substance, such as "oil of wintergreen" (methyl salicylate), or a mixture of odoriferous substances. Another type of "essence" frequently found in fragrances is either plant or animal extracts. Animal extracts include ambergris and musk, while plant extracts include lichens growing on various trees which can be derived from resinous extracts such as terpenes and balsams (2). Mixtures including one, several or many different essential oils and/or extracts are routinely mixed with ethanol and/or water in the manufacture of perfumes and other fragrance products. It is therefore necessary to be able to distinguish and identify the presence of ethanol and water in such mixtures of odoriferous substances.

HTSUS subheadings 3303.00.10 and 3303.00.20 deal with perfumes and toilet waters which contain no alcohol (ethanol) while HTSUS subheading 3303.00.30 describes perfumes and toilet waters which contain alcohol. A footnote to 3303.00.30 also states that imports of perfumes are also subject to a Federal Excise Tax (21 U.S.C. 5001) of \$12.50 per wine gallon. For this reason, it is necessary to determine the alcohol content of the article as well as to determine if the article is or is not a perfume.

Fragrances consist predominantly of water, ethanol and essence and include perfumes, toilet waters, colognes, after-shaves and other lotions, along with products where the fragrances are used as individual components in a more complex mixture such as cosmetics (face creams, lipsticks, powders) and other cleansing aids, including fragrant soaps. The essence can be derived from essential oils and/or plant or animal extracts.

Perfumes are considered to be solutions of essence in alcohol with a minimal amount of water present. Toilet waters generally contain less "essence" than perfumes and contain significant amounts of water. Colognes contain even less "essence" than toilet waters and after-shaves contain still less "essence".

The most important factor to consider when evaluating fragrances is the "essence" content; however, the alcohol and water content must also be considered. Table 1 displays these criteria as reported in two reference sources (See "Reference" Section):

TABLE 1
COMPOSITION CRITERIA FOR FRAGRANCES

-- Fragrance Component Breakdown (Volume Percent) --
 --- Per Reference (3)----- ----Per Reference (4) ---

<u>Fragrance</u>	<u>% Essence</u>	<u>% (95%) Alcohol</u>	<u>% Essence</u>	<u>% (95%) Alcohol</u>
Perfumes	10-25	75-90	10-20	80-90
Toilet Water	2-6	60-80	3-8	75-90
Cologne	2-6	60-80	2-5	70-85
Eau de Cologne (Classique)	---	---	1-3	65-75
Lotion	0.5-2	50-70	---	---
Splash Cologne	0.5-2	50-70	0.5-1	65-75

A method has been developed to identify the presence and amount of ethanol and water in mixtures of odoriferous substances, including fragrances. The method utilizes capillary gas chromatography and thermoconductivity detection (TCD).

The TCD, whose response is dependent upon the difference between the thermal conductivities of the carrier gas and the particular eluting component, demonstrates good linearity for large sample size variations, i.e., for mixtures wherein all the components are of comparable relative concentration ranges. The detector sensitivity and, therefore, the detector response, should be approximately constant. Furthermore, the TCD response is least affected by different component functionality (5).

The detector response is approximately proportional to the concentration of the eluting component in the detector at the time (6), which, at constant flow rate, is approximately proportional to the concentration (weight) of each component in

the sample (7).

The detector also permits the identification of water as well as entrapped gases and various other propellants. The gas chromatogram produced also serves as a "fingerprint" for the product, enabling the verification of genuine samples and the detection of fraudulent products after a simple comparison to reference standards has been performed. The product profile so obtained can also be used to assist the analyst in suggesting in which type of fragrance category the product belongs.

EXPERIMENTAL

A Hewlett-Packard Model 5890 Capillary Gas Chromatograph equipped with a split/splitless Injector, an H-P Thermoconductivity Detector (TCD) and an H-P Model 3390A Integrator was used. The fused silica capillary column consisted of a 30 m. X 0.53 mm. Superox II Polyethyleneglycol column with a 1.2 um. film thickness manufactured by Alltech Associates, Inc., Deerfield, Illinois. Instrument parameters were as follows:

INSTRUMENTAL PARAMETERS

Gas Chromatograph/TC Detector:

Injector Temperature = 250°C
 Column Head Pressure = 4 PSI He
 Split Ratio = ca. 50:1
 TCD Temperature = 275°C
 Initial Temperature = 55°C
 Initial Time = 4.50
 Ramp Rate = 10°C/Min.
 Final Temperature = 220°C
 Final Time = 30 Min.
 GC Attenuation = 0
 GC Range = 1

Integrator:

Peak Threshold = 4
 Area Reject = 8000
 Peak Width = 0.04
 Attenuation = 7/6
 Run Time = 35 Min.
 Chart Speed = 1.0

Approximate Retention times:

Ethanol = 1.3 Min.
 Water = 2.2 Min.

Injection Size will vary between 0.2 uL. for good perfumes and 0.6 uL. for splash and after-shave lotions.

RESULTS AND DISCUSSION

The gas chromatographic scans obtained in each case represented essentially the complete elution of the fragrance sample. This was concluded since no additional components eluted after raising the column temperature to 320°C and also since the results of a gravimetric analysis of a perfume performed after drying it for 30 minutes at 320°C yielded less than 0.2% residue. This amount of residue was not exceeded in any samples tested and was therefore considered negligible and ignored in the analytical calculations.

Gas chromatographic scans of two toilet waters, a concentrated cologne, an after-shave lotion, a genuine perfume and a counterfeit perfume are displayed in Figures 1-6. The area percents obtained from the gas chromatographic scans are equivalent to the weight percent of each component in the

sample and are shown in Table 2:

TABLE 2
RAW INTEGRATION DATA OF VARIOUS FRAGRANCE SAMPLES

Figure	Product Type	Component Area (Weight) Percent		
		%Ethanol	%Water	%Essence
1	Toilet water	68.8	22.6	8.6
2	Toilet water	52.2	28.0	19.8
3	Concentrated cologne	44.8	47.5	7.7
4	After-shave lotion	22.4	72.7	4.9
5	Genuine perfume	45.3	11.9	42.8
6	Counterfeit perfume	59.0	17.8	23.2

The density of the "essence" can be calculated by using the previously and independently determined density of the fragrance sample, D (kg/L), the densities for ethanol and water of 0.794 and 1.000 kg/L, respectively, and the area (weight) percents of each fraction of the fragrance mixture as obtained from the raw integration data:

$$\text{"Essence" Density (kg/L)} = Z = \frac{(100 - A - W)}{(100/D - A/0.794 - W/1.000)}$$

where, A = Area (Weight) Percent Ethanol Peak

W = Area (Weight) Percent Water Peak

D = Overall Density of fragrance sample (kg/L)

The composition of the fragrance sample can be converted to volume percent using the area or weight percents of each component as obtained from the raw integration data, 1.000 kg/L and 0.794 kg/L as the densities of water and ethanol, respectively and by determining the density, Z , of the "essence". This is necessary if the fragrance is ultimately

characterized as a perfume since the ethanol content in volume percent must be determined to calculate the IRS tax.

The component breakdown of these six fragrance samples in volume percent is illustrated in Table 3 and was obtained by using the following formulas to convert composition from weight percent to volume percent:

$$\% \text{ Ethanol} = \frac{(A) (100)}{(0.794) (A/0.794 + W/1.000 + E/Z)}$$

$$\% \text{ Water} = \frac{(W) (100)}{(1.000) (A/0.794 + W/1.000 + E/Z)}$$

$$\% \text{ Essence} = \frac{(E) (100)}{(Z) (A/0.794 + W/1.000 + E/Z)}$$

where, A = Area Percent Ethanol Peak
 W = Area Percent Water Peak
 E = Area Percent Essence Peaks (by subtraction)
 Z = Density of "Essence" Portion (kg/L)

TABLE 3
 COMPONENT BREAKDOWN OF VARIOUS FRAGRANCE SAMPLES

Figure	Product Type	Component Percent by Volume		
		%Ethanol	%Water	%Essence
1	Toilet water	72.7	18.9	8.4
2	Toilet water	56.6	24.1	19.3
3	Concentrated cologne	50.0	42.1	7.9
4	After-shave lotion	26.3	67.8	5.9
5	Genuine perfume	48.9	12.8	38.3
6	Counterfeit perfume	64.1	19.3	16.6

For a review of descriptions and definitions of terms utilized in the fragrance industry which are also applicable to the chemistry of odoriferous substances, see references 8 and 9. There are no distinct differences between currently manufactured toilet waters and colognes other than that the fragrances weaker in essence content are usually referred to as colognes (3). In addition, there are no well-defined differences in the composition of colognes and lotions other than that the fragrances with weaker essence content are usually referred to as after-shaves or lotions. This causes no problem as far as Customs and the Tariff is concerned.

A similar question arises in the classification of fragrances as either toilet waters or perfumes when the essence concentration is relatively high. For these reasons, each product must be considered individually. Before an opinion can be made pertaining to the category of the product, all of its components, that is, the physical, sensory and chemical components, must be carefully considered relative to each other to yield a complete "profile" of the material's characteristics.

Since the chemical component of the material, that is, the alcohol, water and "essence", cannot of itself adequately describe ALL the characteristics of the material, strict chemical specifications for such fragrance categories are therefore very difficult to establish and, therefore, chemical composition of such fragrances obtained using analytical methods as herein described should be used only as an approximate guideline and are to be used along with an appreciation of all of the other properties of the material.

The results in weight percents obtained in Table 2 for the various fragrance samples were obtained directly from the integration of the chromatogram run. Although this format for data display is the most convenient both to obtain and to evaluate, since the characteristics of the various fragrance

categories as displayed in Table 1 are described in volume percents, the results from Table 2 also had to be converted to volume percents. This display of data, illustrated in Table 3, was then compared with the specifications as set forth in Table 1 and finally considered in light of the known final determination that had been rendered on the classification of each specific material as directed by the Classification and Value Division of the U.S. Customs Service.

CONCLUSIONS

Tables 4 and 5 illustrate guidelines, based on this data and the ultimate material classification, which can be used to aid the Customs Officer in the classification of such fragrances when only chemical composition data is available. Table 4 presents these guidelines in volume percent while Table 5 presents them in weight percent. Again, it is most desirable to present this data in weight percent since this data is directly obtained from the integration of the chromatogram:

TABLE 4
VOLUME PERCENT GUIDELINES FOR CLASSIFICATION OF FRAGRANCES
as adopted by U.S. Customs Laboratory, New Orleans, LA

-Component Percent by Volume-			
<u>% Essence</u>	<u>% Water</u>	<u>% Ethanol</u>	<u>Classification</u>
0.1-5.5	1-95	1-50	After Shave/Splash Cologne
3-8	10-80	15-90	Classic or Concentrated Cologne
8-25	16-80	40-90	Toilet Water
10-40	4-15	25-90	Perfume

TABLE 5
WEIGHT PERCENT GUIDELINES FOR CLASSIFICATION OF FRAGRANCES
as adopted by U.S. Customs Laboratory, New Orleans, LA

-Component Percent by Weight-			
<u>% Essence</u>	<u>% Water</u>	<u>% Ethanol</u>	<u>Classification</u>
0.1-5.5	1-95	1-50	After Shave/Splash Cologne
3-8	10-80	15-90	Classic or Concentrated Cologne
8-25	16-80	40-90	Toilet Water
11-45	4-16	20-94	Perfume

The "fingerprint" of the essence as displayed in the gas chromatogram by the pattern of all peaks eluting after three minutes, serves as a means of identification of the fragrance and can be compared using scans obtained from the analysis of bona fide references. As can be seen in Figures 5 and 6, the dramatic differences in these "fingerprints" incontrovertibly established that the fragrance described by Figure 6 is a counterfeit perfume.

This analytical method enables the identification and quantitation of ethanol, water and "essence" in mixtures of odoriferous substances. In addition, a "fingerprint" of the "essence" is obtained which may be used on a technical basis to scientifically perform comparisons of different products. Such technical comparisons can be of great use in the determination of counterfeit products. These technical comparisons can also be of great use, in conjunction with the other physical and sensory properties as previously noted, to enable a classification of the product with much greater confidence. The method, therefore, can resolve identity as well as classification questions regarding fragrances, takes only 35 minutes to perform and utilizes the analytical raw integration data directly without requiring any cumbersome calculations before characterizations of the sample can be undertaken.

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REFERENCES

1. Sax, N.I. and Lewis, Sr., R., Hawley's Condensed Chemical Dictionary, 11th Ed., p. 471, Van Nostrand and Reinhold Co., New York, New York (1987).
2. Ibid., p. 887.
3. Mark, H.F., Mc Ketta, J.J. Jr., and Othmer, D.F., Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 14, p. 739; and Vol. 6 p. 352, Interscience Publishers, New York, New York (1963).
4. Navarre, M.G., The Chemistry and Manufacture of Cosmetics, 2nd Ed., Vol. IV, p. 1034.
5. 1990 Annual Book of ASTM Standards, American Society for Testing Materials, Method E260-85, 14.01, Sect. 6.7 and Sect. 6.7.1 p. 50, ASTM, Philadelphia, PA (1990).
6. 1983 Annual Book of ASTM Standards, American Society for Testing Materials, Method E260-73, 14.01, Sect. 4.6.4.1 p. 386, ASTM, Philadelphia, PA (1983).
7. Dorland, W.E. and Rogers, J.A. Jr., The Fragrance and Flavor Industry, 2nd Ed., p. 65, Wayne E. Dorland Co., Mendham, New Jersey (1977).

8. Bedoukian, P.Z., Perfumery and Flavoring Synthetics, 2nd Ed., p. 124, 162, 171, 240, Elsevier Publishing Company, New York, New York (1967).
9. Guenther, E., The Essential Oils, 3rd Printing, Volume 1, p. 160, Van Nostrand Company, New York, New York (1948).

AUTHORS' COMMENTS:

This monograph is a revision of the original article which appeared in the Customs Laboratory Bulletin, 7(2), 49 (April 1995). Revisions were necessary because the density of ethanol inadvertently used in the original article was 0.816 instead of 0.794. The density of 95% ethanol is 0.816 but does not come into play in any of the mathematical calculations. The density of "100%" ethanol (0.794) must be used in all the mathematical calculations. Because all of the formulas had to be revised to include this corrected density, the compositions by volume of the various substituent components as reported in TABLE 3 also had to be adjusted. In spite of this error, the composition of the various constituent components in the revised table differed by small amounts from previously reported in every instance and the overall guidelines used in the classification of the odoriferous mixtures as illustrated in TABLES 4 and 5 remained unchanged.

The authors resubmit the entire article so that it can be kept in its entirety for reference. We apologize for any inconvenience this oversight may have caused.

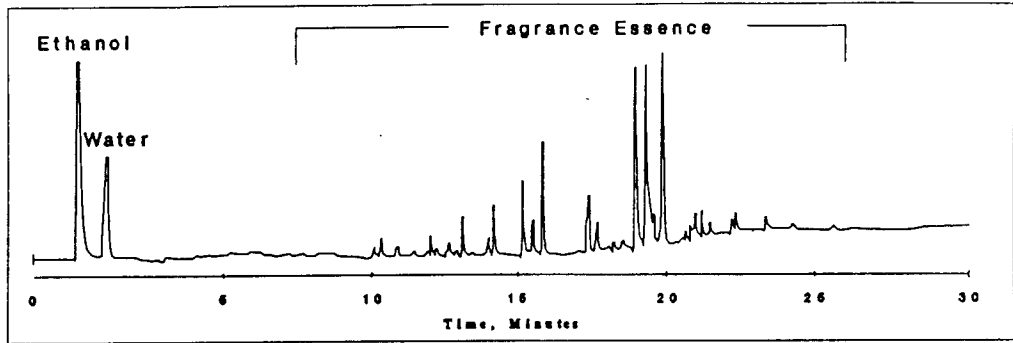


Figure 1. Toilet Water.

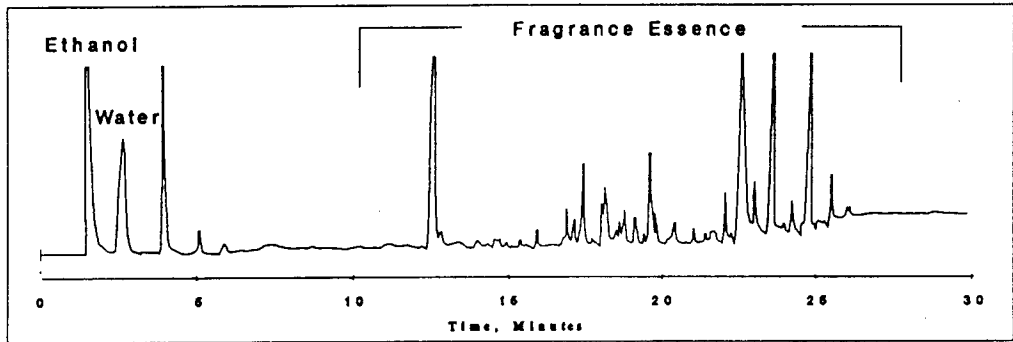


Figure 2. Toilet Water.

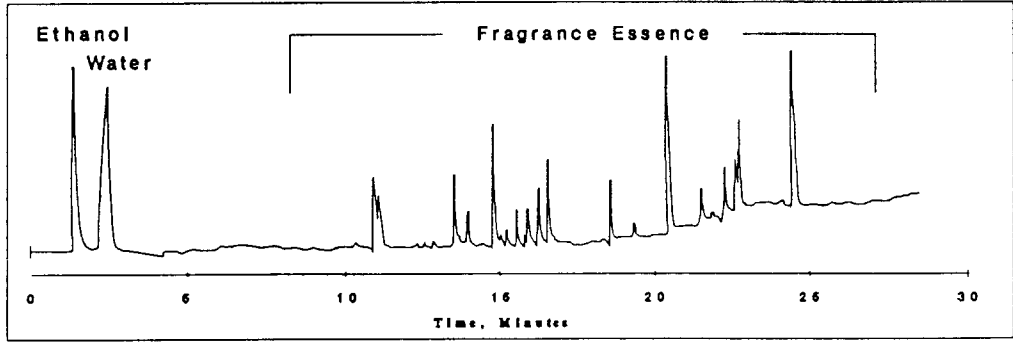


Figure 3. Concentrated Cologne.

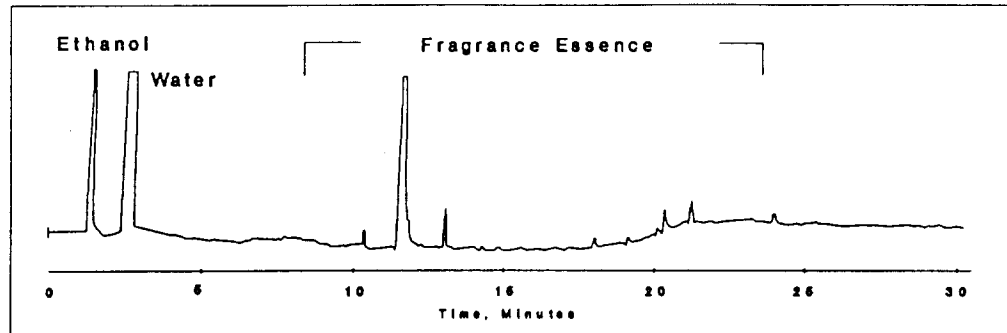


Figure 4. After-Shave Lotion.

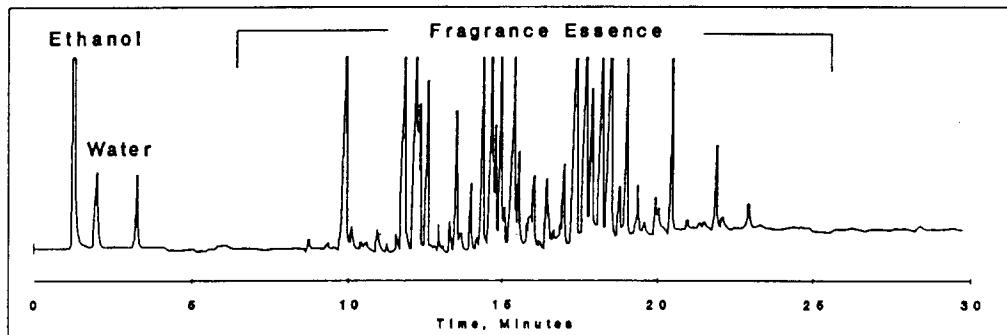


Figure 5. Genuine Perfume.

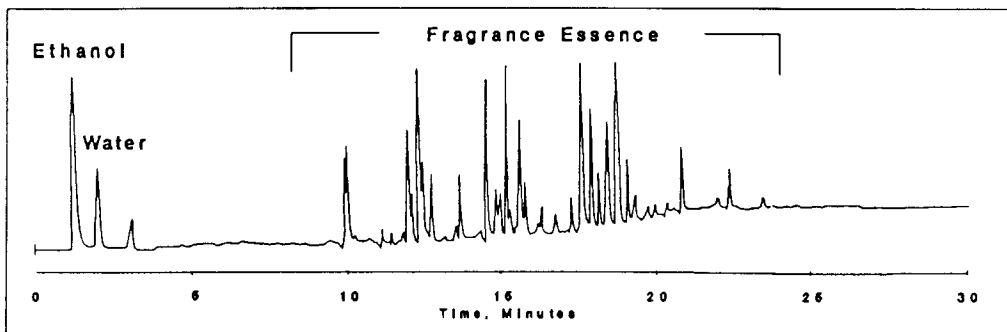


Figure 6. Counterfeit Perfume. Claimed to be that of figure 5.