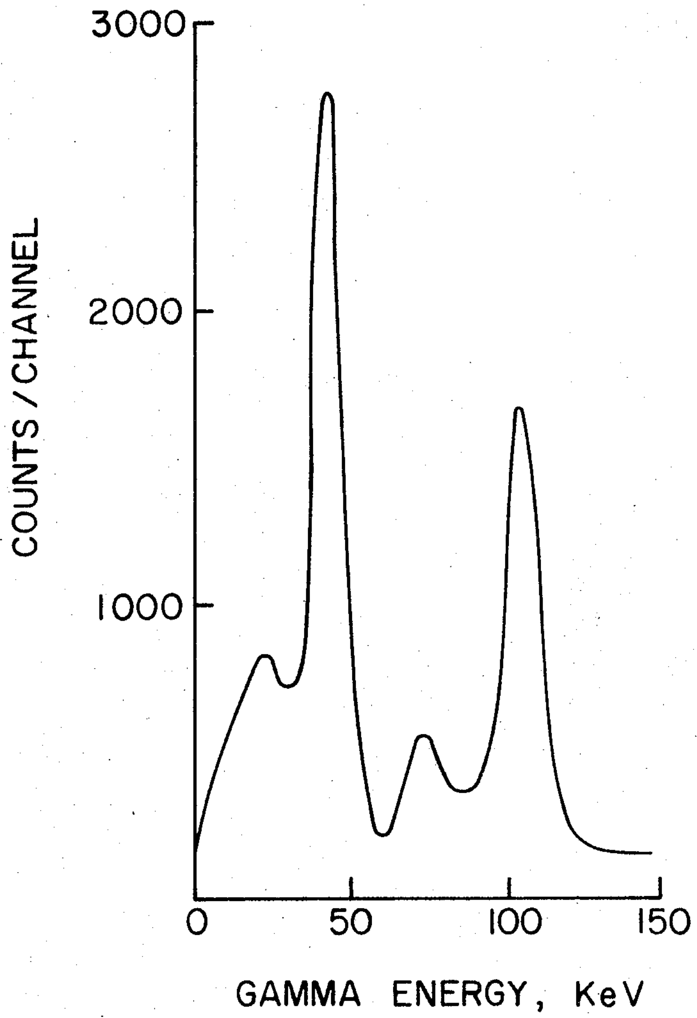
June 29, 1971 M. E. GIBSON, JR., ET AL **3,590,022**

SYNTHETIC POLYAMIDE FIBER CONTAINING SAMARIUM AS A TRACER

Filed Aug. 17, 1967

GAMMA SPECTRUM OF SAMARIUM



INVENTORS
RONALD G. GARMON
MYRON E. GIBSON, JR.

BY Anthony J. Stewart
ATTORNEY

United States Patent Office

3,590,022

Patented June 29, 1971

3,590,022

SYNTHETIC POLYAMIDE FIBER CONTAINING SAMARIUM AS A TRACER

Myron E. Gibson, Jr., Raleigh, and Ronald G. Garmon, Durham, N.C., assignors to Monsanto Company, St. Louis, Mo.

Filed Aug. 17, 1967, Ser. No. 661,419
Int. Cl. C08g *20/20*
U.S. Cl. 260—78 2 Claims

ABSTRACT OF THE DISCLOSURE

Synthetic fibers, such as nylon, polyesters, acrylics, etc., are made unmistakably identifiable by adding samarium, the presence of which, in amounts of between .005 and 50 parts per million, may be detected easily by neutron activation analysis. The samarium that is contained within the synthetic fiber is inactive and does not alter the fiber's chemical or physical properties, since its concentration is extremely low. When identification is desired, a sample of the fiber is exposed to neutron bombardment under standardized conditions and subsequently analyzed.

BACKGROUND OF THE INVENTION

(1) Field of the invention

Synthetic fibers such as nylon, polyesters, acrylics, etc. are rendered unmistakably identifiable by adding an element in trace quantities, the presence of which may be determined easily by neutron activation analysis.

The science of neutron activation analysis (NAA) is relatively new. However, it has been studied extensively since its discovery and has been described in great detail throughout the literature. A comprehensive treatment of this science can be found in "Guide to Activation Analysis," William S. Lyon, Jr., D. Van Nostrand Co., Inc., Princeton, N.J., 1964. The field of activation analysis differs from conventional radioactive analysis in that a stable, or non-radioactive, form of the element is used in very low concentrations and is activated by neutron bombardment prior to analysis. In this way NAA has the advantage that there is never a danger the trace element can be a health hazard to the consumer or user of the product through the emission of harmful radiation.

(2) Prior art

Many products have been tagged with tracers in the past to render them identifiable. Trace elements usually have been detected by conventional chemical analytical methods. Conventional chemical analysis such as titration, colorimetry, emission spectroscopy, etc. have the disadvantage of requiring a relatively high concentration such as more than 100 p.p.m. of the material to effect a positive quantitative identification. Such concentrations have been known to alter the physical and/or chemical properties of the product and render it inferior.

Consequently, this method is unsuitable for the objectives of this invention. Similarly, radioactive tracers suffer from the disadvantage of being a health hazard to the consumer and cannot be used in such applications.

On the other hand it has now been found that neutron activation analysis is a most suitable method that can be used to render a synthetic polymeric product positively identifiable. As stated previously, a considerable body of knowledge is available in this science and certain materials have been introduced into synthetic fiber systems for the

purpose of identification. A workable neutron activation analysis tracer for synthetic fibers must fulfill the following conditions:

(1) Be easily incorporated into the product in a homogeneous manner.

(2) Have no tendency to agglomerate during processing in a manner that would reduce productivity.

(3) Be retained in the product during manufacturing and in subsequent processing into fabric and garments.

(4) Be amenable to neutron activation analysis in the presence of all common interferences in the matrix of the particular fiber or polymer being tagged.

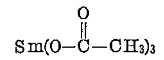
(5) Have a gamma ray spectrum, following activation, that can be identified unambiguously in the presence of residual radioactivity due to the sample matrix.

(6) Be sufficiently sensitive to NAA such that concentrations may be employed which will not significantly increase the cost of the product.

It will be shown subsequently that these conditions are fulfilled by this invention.

SUMMARY OF INVENTION

In accordance with this invention there is provided a synthetic fiber containing between 0.005 and 50 parts per million of added samarium. It has been found that it is possible to identify positively the source of synthetic fibers by adding between 0.005 and 50 parts per million of samarium, preferably in the form of samarium acetate,



$$Sm(O-\overset{\overset{O}{\|}}{C}-CH_3)_3$$

to the polymer system prior to fiber manufacture. The concentration of samarium required for positive identification of the resulting synthetic polymeric product is so low that the product properties are unaffected. Yet samarium can be detected quantitatively at these extremely low levels by seubsequent neutron activation analysis.

Generally the samarium is added as a salt, (e.g.) samarium acetate, or as the oxide, samarium oxide. In aqueous systems such as 66 nylon salt the acetate is preferred. In other systems it may be desirable to suspend an insoluble form such as the oxide, which is preferred for use in acrylic or spandex dopes. Among the fiber-forming polymers to which this invention is applicable are: polyesters, polyvinyl chlorides, cellulosics, polycarbonates, polyolefins, polyamides, ordered polyamides, and the like.

While 5 p.p.b. (0.005 p.p.m.) of samarium can be used for qualitative identification, preferably, at least about 50 p.p.b. (0.05 p.p.m.) of samarium is employed for easy quantitative measurements by neutron activation analysis. Concentrations above 50 p.p.m. are not desirable since this level is more than enough for most measurements and polymer property modification at this level and below is avoided entirely. The preferred concentration of samarium is from about 0.005 to 5 parts per million parts of polymeric material, with concentrations of from about 0.1 to 5.0 p.p.m. being most preferred.

Surprisingly, it has been found that samarium is not only desirable, but unique, when used as a trace element in synthetic polymeric products for positive identification by neutron activation analysis. This will become evident as is illustrated below.

Many elements in various forms may be incorporated into synthetic fibers to provide a subsequent successful activation analysis. Examples of such elements are gold, indium, holmium and many others. However, all suffer from serious disadvantages, such as (1) an unfavorable half life or (2) a high concentration needed for detection, or (3) abundance as an impurity in nature or (4) they do not possess a unique spectrum free of interference. If any one or more of the above mentioned disadvantages is present in a system an uncertain identification can result from the analysis.

The term, "half life" as used herein, is defined as the time necessary for the activity of the system to decrease to 50 percent of its initial level. The symbol $t_{1/2}$ is used herein to designate this property. Should the half life of the active species be unduly short, subsequent analysis would be difficult, if not impossible due to the time needed for sample preparation. Conversely, if the half life of the activated species system were too long it would require extremely long activation times.

In actual practice the total activity of a freshly activated system excessive because many elemental species present as impurities or additions are activated in addition to the tracer element. Fortunately, the half lives of the most common impurities in fibers such as sodium, manganese, etc. are sufficiently short such that their collective activity approaches zero after delaying the counting a few hours or so, while the activity of samarium is still relatively high due to its favorable half-life of about 47 hours. This delay permits efficient monitoring of the intended tracer whose intensity is still high and contributes to the unmistakable identification of the substrate.

If extremely high concentrations of the element are needed for detection there is the risk that the properties of the substrate may be affected. In using samairum it has been found quite unexpectedly that the very broad range of 0.005 to 50 parts per million can be used. This broad, usable concentration range is particularly valuable since the sample size needed for detection can be very small, such as in individual filaments (2–6 denier) from staple, or it can be relatively large such as in heavy denier monofil, yet the same trace element can be used by simply adjusting its concentration. In general, it is possible, and sometimes preferable, to employ a higher samarium concentration for low denier fibers and use a lower concentration for higher denier fibers. Furthermore, the broad concentration range will allow the user to index fibers on the basis of manufacturing location, or some other desirable variable, by quantitative neutron activation analysis. A scheme can be devised whereby a level of 0.5 p.p.m. samarium was manufactured at location A, 1 p.p.m. at B, 2 p.p.m. at C and so on, thereby greatly extending the utility of this invention.

As stated previously another advantage in using samarium in neutron activation analysis system is that it will never be found as a contaminant in the substrate at levels high enough for detection. This is evident from the fact that samarium is a rare earth and occurs in very minute quatities in such minerals as samarskite and cerite which are unusual throughout the surface of the earth. Consequently, the probability of samarium's being present in a substrate by chance is nil, again allowing identification of the substrate to be unmistakable.

But most importantly, the γ-ray spectrum of samarium is unique and consequently unmistakable. This spectrum is shown in the drawing. It can be seen from the drawing that there are two sharp emission peaks, one at about 41 kev. and the other at about 102 kev. having about 2750 and 1680 counts/channel respectively, and having a peak height ratio of about 0.61. The location of these peaks serve as positive identification for samarium. Therefore, the principle utility of this invention is the unmistakable identification of a synthetic fiber product which contains samarium as the trace element and can be subjected to neutron activation and subsequent analysis.

PREFERRED EMBODIMENT

EXAMPLE I

The following example is a preferred embodiment of this invention. The example describes the preparation of samarium acetate from the oxide and the subsequent use of the acetate in 66 nylon preparation.

Preparation of samarium acetate

A suspension of 348 g. (one mole) of Sm_2O_3 in 2 l. of glacial acetic acid was heated at reflux for one hour. Two liters of water were added to the suspension. The resulting solution was diluted with water to 0.1131 molar $Sm(OAc)_3$.

Preparation of nylon fiber containing samarium

Twenty milliliters of the above solution (about 0.1131 molar) was added to a solution of nylon 6,6 salt, i.e., hexamethylene diammonium adipate, sufficient to prepare 2500 pounds of nylon 6,6 polymer, i.e., polyhexamethylene adipamide. Polymerization was carried out by the usual, well-known method. Fibers spun from the above polymer were found to contain approximately 280 (0.28 p.p.m.) parts per billion samarium.

Extraction of Sm from nylon fiber

In a series of extraction experiments 3 g. samples of the above fiber were extracted at reflux for one hour with 200 ml. portions of carbon tetrachloride, water, and solutions (0.5 g./l.) of the following material: sodium hydroxide, sodium carbonate, sodium phosphate, ammonium acetate, formic acid, acetic acid, phosphoric acid. In all cases analysis after extraction showed no loss from the fiber of Sm within the precision of the measurement.

Neutron activation analysis

At the 200–300 p.p.b. level neutron activation analysis for Sm is strictly an instrumental technique, i.e., no chemistry, such as sample concentration, etc., is required.

The technique involves irradiation of the sample in a thermal neutron flux for a given period of time. Use a 2 hr. irradiation at a flux density of about 10^{11} neutrons cm.$^{-2}$ sec.$^{-1}$. The gamma specrum of the sample resulting from this irradiation is then measured. The energy and half-life of the gamma radiation is characteristic of each element, although many elements exhibit similar characteristics.

The moderately long half-life of the resulting samarium-153 (47.4 hr.) is especialy useful in that many of the other activated species of shorter half-lives may be allowed to decay before measuring the gamma spectrum, thereby simplifying the analysis for Sm-153.

EXAMPLE II

This example illustrates the use of samarium by the addition of the acetate salt to a polyester system.

Preparation of polyethylene terephthalate (PET) fiber containing samarium

One milliliter of the samarium acetate solution prepared as described in Example I was added to a slurry of ethylene glycol and terephthalic acid sufficient to prepare 34.7 pounds of PET. Polymerization was carried out by the usual , well-known method. Fibers spun from the above polymer were found to contain approximately 1.1 p.p.m. samarium.

Extraction of Sm from PET fiber

A 2 g. sample of PET fiber prepared similarly to the above PET fiber and containing 1.6 p.p.m. Sm was scoured 20 minutes at 90° C. with a mixture of Varsol[1], soap and water and containing 0.1 weight percent NaOH. Analysis after extraction. showed no loss from the fiber of Sm within the precision of the measurement.

What is claimed is:

1. As an article of manufacture a polyhexamethylene adipamide fiber containing on a weight basis, as an identi-

---

[1] Trademark Esso Standard Oil Co. long chain aliphatic HC w./flash point about 100° C.

fiable tracer, from about 0.005 to 5 parts of samarium, added as the acetate or oxide thereof, per million parts of said fiber.

2. The article of claim 1 wherein the samarium is added as samarium acetate.

References Cited

UNITED STATES PATENTS

2,643,989	6/1953	Auspos et al.	260—75
3,166,431	1/1965	Mullaly	260—429.2
3,189,620	6/1965	Smutny	260—45.75
3,254,103	5/1966	Melby et al.	260—429.2
2,497,546	2/1950	Griffin	106—237

OTHER REFERENCES

Floyd Polyamide Resins, second edition, 1966, p. 14.

HAROLD D. ANDERSON, Primary Examiner

U.S. Cl. X.R.

250—106; 260—47, 75, 77.5, 92.8, 93.1, 212