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2,646,522

CATHODE-RAY CENTERING

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3 Claims. (Cl. 313-77)

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This invention relates to magnetic apparatus and more particularly to magnetic beam adjusting arrangements for cathode ray tubes and the like.

The generally accepted arrangement for producing beam deflection in cathode ray tubes has been the application of electromagnetic or electrostatic fields to the cathode ray at a position between the source of electrons and the target area.

Heretofore there has usually been recourse to various ways and means by which there is provided a direct current flow through the deflecting coils in such a way as to develop a field to provide adequate centering or locating of the cathode ray beam. An example of this type of apparatus is found in U. S. Patent 2,007,380 to W. J. Morlock, dated July 9, 1935. Such methods, although proving very satisfactory, nevertheless tend to introduce objectionable resistance into the deflecting circuit and also tend to demand a relatively high current drain through the centering potentiometer. Very low impedance yokes cannot, therefore, for practical reasons be used for deflection under such circumstances because of the relatively high centering current requirements.

There have also been proposed arrangements for overcoming the necessity for maintaining a continuous direct current flow through the deflection electromagnet of the cathode ray tube. Such arrangements have employed permanent magnets whose magnetic field is arranged to act in connection with the deflection field to provide a continuous deflection field in a desired direction and thus to accomplish centering. Arrangements for varying the magnitude and the direction of the magnetic field furnished by the permanent magnet have been suggested, such as a magnetic shunting ring closely adjacent to the permanent magnet. An example of this type of apparatus may be found in the U. S. patent to H. B. Kuehni, No. 2,102,421, dated December 14, 1937.

It is this latter class to which this invention is specifically directed. According to this invention, two rings of a suitable magnetic material are mounted on the neck of the tube and arranged so that they can each be rotated through 360°. The rings are magnetized in such a manner that they each produce lines of flux at right angles to the path of the beam. When the rings are rotated with respect to each other so that the flux fields are aiding, maximum centering action is obtained, and when they are turned so that the flux fields are closed, practically zero centering

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action is obtained. Any desired degree of centering action between zero and maximum may be obtained by rotating one ring with respect to the other. The direction of this centering action may be altered as desired by rotating both rings together.

A primary object of this invention is to provide an improved electron beam centering means which will not require any flow of electrical energy but which at the same time will provide a system which is readily adjustable to control the beam centering.

Another object of this invention is that of providing an arrangement where adequate and proper centering or positioning of the electron beam within a cathode ray tube may be provided and still permit the use of a substantially cheaper yoke construction with many fewer turns than those now customarily in use.

Other and incidental objects of the invention will be apparent to those skilled in the art from a reading of the following specification and an inspection of the accompanying drawing in which:

Figure 1 shows schematically one form of this invention;

Figure 2 illustrates an end view of a section including the magnetic rings of Figure 1; and

Figure 3 illustrates another view of the form of the invention shown in Figure 1.

Turning now in detail to Figure 1, there is shown a cathode ray tube 1, including the usual electron gun 3 and the target area of luminescent screen 5.

Cathode ray tube 1 is provided with magnetic deflection coils 7 which are arranged in the usual manner to provide both horizontal and vertical deflection. The practice of the present invention is also operable to electrostatic deflection.

Details regarding the cathode ray tube 1 and its associated elements are not given here, but may be found well described in the cathode ray tube and television art. The "kinescope," as the cathode ray tube in television is normally called, as well as associated circuits, is described in detail in the book entitled "Principles of Television Engineering" by Donald G. Fink. An improved cathode ray tube is shown and described in an article entitled "Improved Cathode Ray Tubes With Metal-Backed Luminescent Screens," published in the "RCA Review" for March, 1946.

The path of the electron beam is appropriately illustrated by line 9.

According to this invention, there is positioned about the neck 10 of the tube 1 a pair of magnetic

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PROCESS OF COMBATING FUNGI WITH A PINONIC ACID DERIVATIVE AND A COMPOSITION OF A CELLULOSE ESTER AND SAID DERIVATIVE

Torsten Hasselstrom, Philadelphia, Pa.

**No Drawing. Application September 15, 1950,
Serial No. 185,137**

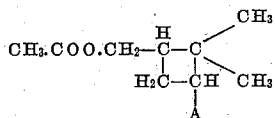
9 Claims. (Cl. 106—174)

(Granted under Title 35, U. S. Code (1952),
sec. 266)

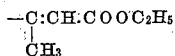
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The invention described herein, may be manufactured and used by or for the Government for governmental purposes, without the payment to me of any royalty thereon.

The objects of this invention are processes of combating fungi with derivatives of pinonic acid, and to their application in the plasticizing of lower alkanoyl cellulose esters. These pinonic acid derivatives are the methyl ester of pinonic acid and the methyl ethyl diester of 1-methyl homodehydroethylene pinic acid synthesized therefrom. These two compounds can be represented by the structural formula



wherein A is $-\text{CO}\cdot\text{CH}_3$ in the case of the methyl ester of pinonic acid, and



in the case of the methyl ethyl diester of 1-methyl homodehydroethylene pinic acid.

I have found that certain higher esters of terpene carboxylic acids are excellent plasticizers and possess other valuable properties such as being fungistatic; this discovery as well as the preparation of these esters is set forth in my co-pending application Serial No. 185,139 "Terpene Carboxylic Acid Esters," filed September 15, 1950. I have further found that the methyl ester of pinonic acid and its derivative, the methyl ethyl diester of 1-methyl homodehydroethylene pinic acid likewise possess these properties.

A commercially practical method for producing the methyl ester of pinonic acid is the oxidation of distilled turpentine (alpha pinene) to form crude pinonic acid and the esterification of the pinonic acid thus obtained with a methylating agent. The reaction product, the methyl ester of pinonic acid is preferably isolated by fractionation. Reaction of the methyl ester of pinonic acid with ethyl bromoacetate and zinc (or magnesium), in accordance with the general pattern of the Reformatsky reaction, followed by dehydration yields the methyl ethyl diester of 1-methyl homodehydroethylene pinic acid.

The following examples illustrate the production of typical pinonic acid derivatives contemplated by the present invention:

EXAMPLE I

Methyl ester of pinonic acid

150 g. alpha-pinene was emulsified by mixing in 3000 cc. of water, and 232 g. of potassium per-

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manganate added with efficient stirring, in portions, during a period of about four hours. The temperature was kept below 20° C. and the stirring continued for four hours additional. After standing overnight, the color of the permanganate had disappeared. The manganese dioxide formed in the reaction was removed by filtration, the precipitate washed with about 300 cc. of water, and the clear filtrate evaporated in a stream of carbon dioxide until approximately 500 cc. of brown syrup remained. This residue was acidified with dilute sulfuric acid, whereby the terpene carboxylic acids separated as an upper, oily layer, which was separated by gravity from the lower aqueous layer containing potassium sulfate and free sulfuric acid. Yields of terpene carboxylic acids, crude pinonic acid, were approximately 50% by weight of the starting material, alpha-pinene.

20 In order to recover maximum amounts of
terpene carboxylic acids, the aqueous lower layer
was extracted with ethyl ether, the ether solu-
tion dried with anhydrous sodium sulfate, and
the ether distilled off, whereby the residue repre-
25 sents the total amount of terpene carboxylic
acids produced. Instead of ethyl-ether any
water-immiscible solvent may be used, in which
the terpene carboxylic acids are soluble as, for
instance, chloroform, tetrachloroethane, ethyl-
30 enedichloride, aliphatic hydrocarbons, benzene
and its homologs, aliphatic and aromatic ethers
and esters. In the acidification step, hydro-
chloric acid, phosphoric acid, acid sodium sul-
fate and the like might be used instead of sul-
35 furic acid.

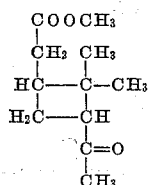
While potassium permanganate was employed as the oxidation reagent for turpentine in this example, other oxidizing agents may be employed for the making of terpenecarboxylic acids from turpentine as, for example, sodium permanganate, alkali and alkaline earth dichromates, alkylferrocyanides, sulfomonoperacid, and the like. Furthermore, ozonation, auto-oxidation, oxidation with air or oxygen under pressure, in the presence of alkali and catalysts as, for example, manganese salts, electrolysis, etc., may be employed; but for securing high yields of terpenecarboxylic acids, intermediate compounds such as alcohols, glycols and aldehydes may have to be subjected to a reoxidation.

The methyl ester was then prepared as follows: 100 g. terpene carboxylic acids (crude pinonic acid) was dissolved in 100 cc. of water containing 43 g. sodium hydroxide. To the solution was added at room temperature 114 g. dimethylsul-
55 fate with good stirring. Upon completion of the reaction the mixture was heated on a boiling water bath for about two hours; the upper ester layer separating by gravity from the lower aque-

ous layer. The mixture was extracted with ether. The residue after evaporation of the ether was fractionated in vacuum, and the fraction boiling at about 75–79° C. (400 μ) was then collected. Yield 30.9 g. of highly refined methyl ester of pinonic acid: refractive index $n_D^{20}=1.4579$; $n_D^{25}=1.4561$; specific gravity

$$d_4^{20}=1.02638$$

Structural formula:



For further identification the semicarbazone of the methyl ester of pinonic acid crude pinonic acid was prepared in the conventional manner. This semicarbazone melted at 148–150° C.

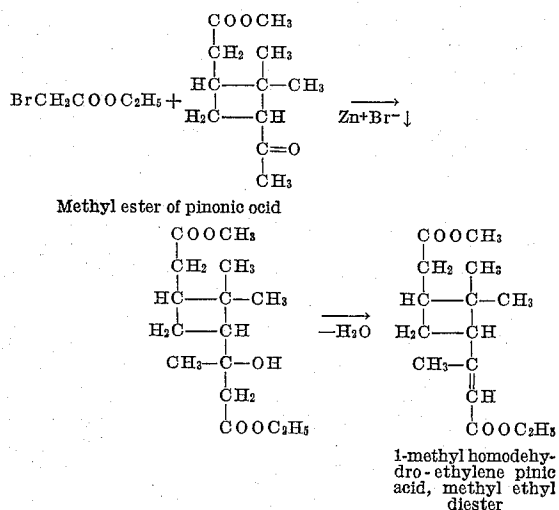
In large scale operation the isolation of crude terpene carboxylic acids may be omitted, inasmuch as the brownish syrup resulting from the potassium permanganate oxidation may be directly treated with dimethylsulfate.

EXAMPLE II

Methyl ethyl diester of 1-methyl homodehydroethylene pinic acid

19.8 g. ($\frac{1}{10}$ mol) of the methyl ester of pinonic acid obtained from the procedure of Example I, 16.7 g. ($\frac{1}{10}$ mol) ethyl bromoacetate, and 6.5 g. ($\frac{1}{10}$ mol) of metallic-zinc were covered with about 75 cc. of benzene and jointly warmed. After the reaction started, it was permitted to proceed for $\frac{1}{2}$ hour, and the reaction products were then refluxed by exterior heating. After about 5 hours, the zinc-containing precipitate was filtered off. About 0.19 g. of benzene sulfonic acid were then added to the solution, and the whole was refluxed for approximately 48 hours, and split off water was collected in a water trap. The reaction product was subjected to fractional distillation, and the fraction having a boiling point of 165–184° C. at 10.5 mm. Hg pressure was collected. This fraction, the methyl ethyl diester of 1-methyl homodehydroethylene pinic acid is a dark brown oil, refractive index $n_D^{20}=1.982$. The yield was about 20%.

The course of the Reformatsky reaction may be represented as follows:



It will be understood that homologs and analogs of the methyl ethyl diester of 1-methyl homodehydroethylene pinic acid may be prepared from the ethyl ester of pinonic acid with the Reformatsky reaction, by substituting equimolecular proportions of ethyl and other lower alkyl esters of alpha-bromo-aliphatic acids for the ethyl bromoacetate of this example.

In comparative tests for the fungistatic properties of the products prepared in accordance with the preceding examples, they were added to Czapek's agar solution (concentration of 250 p. p. m.); the solutions were placed on test plates, inoculated with *Aspergillus niger*, TC215–4247, and incubated for 96 hours at 85–90° F. and 85–90% relative humidity. The results were computed in terms of per cent of inhibition, based on the average diameter of the fungus colonies of the test plates as compared to that of the untreated controls. The results are shown in the following table:

Compound	Percent Inhibition
Methyl ester of pinonic acid	26
Methyl ethyl diester of 1-methyl homodehydroethylene pinic acid	55
These results compare with those obtained with conventional fungistatic agents as follows:	
Methyl salicylate (winter green oil)	12
Benzic acid	42
n-Hexyl benzoate	48
Salicylic acid	40

The methyl ester of pinonic acid shows a remarkably low pour point (freezing point): –77° C. Tests for evaluating the performance of the methyl ester of pinonic acid as a plasticizer fully bore out the expectations raised by its favorable pour point characteristics. The tests were carried out by preparing a stock solution of 70 g. of lower alkanoyl cellulose ester in 1000 g. of organic solvent, and adding the methyl ester of pinonic acid in the ratio of 1 part of methyl ester of pinonic acid to 4 parts of stock solution. 25 g. portions of each plasticized solution were poured into Petri dishes of 9.5 cm. diameter, and the solvent was allowed to evaporate over a period of approximately 3 days.

Per cent shrinkage was computed after formation of the film by determining the ratio of the uncovered area of the Petri dish with its total area. Per cent shrinkage of less than 3% should be considered negligible in actual practice.

Flexibility at room temperature (20° C.) was determined by folding 1 sq. cm. of the film on an axis first in one direction and then in the opposite direction. The film is folded again on an axis which is perpendicular to the first axis in one direction and then again in the opposite direction. Any break in the film caused it to be considered non-flexible. To determine the flexibility below –50° C., 1 sq. cm. of the film was placed in a test tube, which was immersed in a Dry-Ice acetone bath. After a period of approximately five minutes, the film was tested for flexibility as previously described.

The following results were obtained with Cellulose Acetate PM-3 (Hercules Powder Company): Clear film without shrinkage, flexible at 20° C. and below –50° C. With Cellulose Propionate—Formula No. 28,251 (Celanese Corp.), a clear film with 3% shrinkage, and flexible at 20° C. and below –50° C. was obtained.

In comparative tests to determine the effectiveness of commercial plasticizers on cellulose esters at low temperatures it was found that Cellulose