Patented June 6, 1939 2,160,929

UNITED STATES PATENT OFFICE

2,160,929

HERBICIDAL OILS

James Prince Warner and Alexis Voorhies, Jr., Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application October 3, 1935, Serial No. 43,384

4 Claims. (Cl. 167—45)

This invention relates to herbicidal oils and relates particularly to herbicidal oils that are of special value in the control of perennial weeds such as burdocks, dandelions, Bermuda grasses, and other growths having a deep underground root system. These herbicidal oils are also especially useful, besides killing the perennial weeds, in preventing the growth of these perennial weeds, and other undesirable growths.

According to this invention highly toxic herbicidal oils are prepared from mineral oils. These herbicidal oils are preferably produced by the destructive hydrogenation of mineral oils, the mineral oil being either a straight run or cracked oil or an oil made by selective extraction of a straight run or cracked oil. The oils from which these herbicidal oils are derived may be of a boiling range including that of gasoline and extending up to 700° F. or somewhat higher. In addition to destructive hydrogenation, other methods of producing these herbicidal oils are high temperature cracking of liquid or gaseous hydrocarbons or mixtures thereof, or selective extractions of suitable base stocks. Herbicidal oils so produced are found to contain a substantial amount of aromatic hydrocarbons together with naphthenic and unsaturated hydrocarbons.

In the preferred destructive hydrogenation process, these distillate oils as such or fractions separated by the use of selective solvents, are passed in vapor phase with hydrogen over suitable catalysts at a pressure in excess of 20 atmospheres and preferably at a pressure of 100 to 200 atmospheres or higher, and at a temperature above about 900° F. and preferably within the range of about 930°–1050° F. with a suitable partial pressure of hydrogen and time of contact to secure destructive hydrogenation without the formation of appreciable amounts of polymerized or coky material.

The hydrogen recycled with the oil is preferably within the range of 1,000–10,000 cubic feet per barrel of feed oil and the hydrogen consumed is preferably within the range of 500–2500 cubic feet per barrel of feed oil, the amount generally depending upon the gravity and boiling range of the charging stock.

A greater proportion of hydrogen may be used with suitable variation in feed rate, temperature and pressure as is known in the art. The feed rate depends upon the reaction temperature and other operating conditions, such as the partial pressure of hydrogen, and may be suitably about 0.75 to 4 volumes of oil per volume of catalyst filled reaction space per hour. The catalysts preferably comprise the oxides or sulfides of the metals of the VI group of elements with suitable promoters of the alkaline earth and earth oxides. Such catalysts are insensitive to sulfur poisoning and are suitably classified as sulf-active.

The product of such vapor phase destructive hydrogenation of petroleum distillates or hydroforming process is called a "hydroformed oil" for the purpose of this invention and the claims.

This hydroformed oil is fractionated and the fraction having a low aniline point such as 20° F. to —80° F. and a gravity of about 8 to 20° A. P. I. has been found most suitable as a herbicidal oil. Extractives obtained by extracting suitable base stocks with selective solvents and having similar aniline points are also suitable for use as herbicidal oils. Highly cracked oils from suitable base stocks having similar aniline points are also suitable for use as herbicidal oils. The oils that contain substantial amounts of aromatic hydrocarbons were found to be more effective than oils that are olefinic. Aniline points lower than the freezing point of aniline are determined by mixing the low aniline point oil under test with an oil of known and relatively high aniline point and calculating or determining by graphical extrapolation the unknown low aniline point from that of the mixture.

These herbicidal oils were found to have toxicities between 0.01 and 0.02% when compared with the toxicity of coal tar creosote tested by the same method and whose toxicity is usually about 0.05%. These herbicidal oils were therefore found to be more toxic than coal tar creosote by this method of test. The toxicity tests on the wood preservatives were made in nutrient agar medium with the standard fungus "fomes annosus". Of the herbicidal oil used in the above case, nearly 90% distills between 392° and 518° F. When all the oil is distilled up to 639° F. there is still a small residue but there is no strong indication of decomposition. The oil is completely sulfonated by sulfuric acid of the strength usually recommended for this test on creosote, that is, it shows no evidence of containing any large amounts of paraffin hydrocarbons.

These herbicidal oils may be further treated and part of the hydrocarbons converted into phenolic bodies by any of the well known methods, such as fusion of the sulfonates with caustic potash or by the diazo reaction, and the resulting phenolic compounds may be isolated in a partially purified form and mixed with a residual highly cracked hydrogenated or unhydrogenated cycle stock to give a mixture that closely resem-

bles coal tar creosote. Petroleum products or other products of a pitchy nature or merely of a high boiling range may also be added to the mixture in order to obtain a resultant mixture which is effective over a longer period of time, and which, for example, may contain a residue above 671° F. which varies between 5 and 50% of the resultant mixture.

These herbicidal oils may be further treated to increase their efficiency, i. e. by the addition of small amounts of phenols, cresols, etc. or the following substances which are principally compounds of arsenic, copper or mercury: Copper naphthenate; copper sulfonate; diphenylamine chlorarsine; phenyl arsinous oxide; mercuric oxide; mercuric chloride; mercuric arsenate; cuprous cyanide; cupric orthonitrobenzoate; mercuric anilenate; crystal violet; methylene blue. Alternately small amounts of substances such as alpha- or beta- naphthol increase the toxic efficiency of the higher boiling fractions which are preferably used.

These herbicidal oils are sprayed over the weeds and at least 3 to 4 ounces are used for every 100 square feet of surface. Usually two or three applications are sufficient to kill all the weeds. After the weeds are once all killed off about three or four applications a year are sufficient to keep the surface free of weeds. These herbicidal oils are also toxic to insects and larvae. They readily spread when applied to the surface of water and owing to their high boiling points are effective over a long period of time. When sprayed over the ground in preparation for construction they can be used to kill off the vegetation together with the termites, etc. as the herbicidal oils are of low viscosity and will readily soak into the ground. When used on insects other insecticidal ingredients may be added, for example pyrethrum and derris extracts.

These herbicidal oils are especially useful in controlling marine growth when used alone on fish nets, ropes, etc. or incorporated in marine paints. The herbicidal oils when used in marine paints are preferably used together with some of the above compounds of arsenic, copper and/or mercury. Nets and ship bottoms when treated with these herbicidal oils are kept free of marine vegetation and also other undesirable growths such as barnacles, etc. The herbicidal oils used in paints, etc. can be first resinified for example, by condensation with ethylene dichloride in the presence of aluminum chloride. A partial resinification of these hydrogenated and highly cracked fractions results in a product containing sufficient polymerized and condensed molecules to ensure a tough film, but also containing enough of the lower boiling substances to impart considerable toxicity.

The foregoing description is merely illustrative and various changes and alternative arrangements may be made within the scope of the appended claims in which it is our intention to claim all inherent novelty in the invention as broadly as the prior art permits.

We claim:

1. A herbicidal hydroformed petroleum oil of an aniline point of about 20° to —80° F. and a gravity of about 8° to 20° A. P. I.

2. A herbicidal oil comprising a hydroformed petroleum oil composed substantially of aromatic, naphthenic, and unsaturated hydrocarbons and having an aniline point of about 20° to —80° F. and a gravity of about 8° to 20° A. P. I.

3. A herbicidal oil comprising a petroleum oil fraction obtained by the use of a selective solvent and composed substantially of aromatic, naphthenic and unsaturated hydrocarbons having an aniline point of about 20° to —80° F. and a gravity of about 8° to 20° A. P. I.

4. A herbicidal oil comprising a liquid product composed substantially of aromatic and unsaturated hydrocarbons having an aniline point of about 20° to —80° F. and a gravity of about 8° to 20° A. P. I. and obtained by hydrogenating a petroleum oil.

JAMES PRINCE WARNER.
ALEXIS VOORHIES, JR.