

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Bittering Agents for Malt Beverages

We, MILLER BREWING COMPANY, a Corporation organised and existing under the laws of the State of Wisconsin, United States of America, of 4000, West State Street, Milwaukee, Wisconsin, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of bittering agents for malt beverages such as beer and ale. In particular it relates to a process of preparing bittering agents for such beverages, to the bittering agents so prepared to such a beverage when containing such a bittering agent and to the preparation of such a beverage.

It is well known that beer and ale and similar malt beverages are produced from water, barley malt, adjuncts and hops. The malt and adjuncts furnish the carbohydrates and other growth essentials which make up the wort. This wort, boiled with hops, in turn forms the basic substance for fermentation in the fermenting tanks. The hops give the characteristic bitter flavor and pleasant aroma to the beer. They assist in preserving the beer and improve its foam holding capacity.

Unfortunately, beer and ale and other similar malt beverages are not stable to light. Light of both visible and invisible wave lengths affects them adversely producing actinic damage in the form of a characteristic skunky odor. Such a beer is commonly known as "light struck". The actinism is caused by chemical changes, producing compounds probably mercaptanous in nature. Tests show that the olfactory threshold level of odiferous compounds of this character is very low, in the range of a few parts per billion. This shows clearly the acute nature of the problem.

Many efforts have been made in the past to

overcome this difficulty. Much time has been expended on packaging of beer and ale to exclude light. Colored bottles have been used and opaque packages are common. It is not uncommon to label them "Do Not Expose to Light".

We have discovered a way to overcome the hazard of product exposure to light which forms the basis of our invention, and have thereby achieved a substantially anactinic malt beverage. The term "anactinic" is intended to succinctly describe a beverage which will not be subject to actinic damage. The word is herein coined and is derived from the word "actinic" plus the prefix "an", meaning "not".

We have found that three factors are necessary for the reaction causing malt beverages to become light struck. They are photo energy in the wave length region of 1000 to 10000 Angstrom units, a sulfhydryl bearing compound, and a chemical component derived from the raw materials, hops, during the brewing process.

The primary object of the invention is to provide a hop extract and malt beverage that is stable to light and will not produce unpleasant olfactory characteristics.

A further object of the invention is to so treat the hops in malt beverages so as to retain the aroma, bouquet and bitterness in the finished product, but eliminate the photoactive elements thereof.

A still further object of the present invention is to provide a method of treating hop extract in the presence of a reducing agent to provide a concentrated product having particular application in malt beverages production, whereby its use will not affect the desired characteristics of the beverage, but will eliminate photoactive elements therein.

According to one aspect of the present invention there is provided a process for pre-

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paring a bittering agent for a fermented malt beverage such as beer or ale in which process hops are treated to render constituents of the bittering agent, normally chemically reactive with the sulphhydryl groups normally present as a component in such a malt beverage, chemically inactive towards said sulphhydryl groups, so that the bittering agent when combined with the ingredients of said beverage provides a light-stable product free from those chemical effects of actinic attack which would otherwise cause said product to have objectionable light-struck characteristics.

According to another aspect of the present invention there is provided a fermented malt beverage such as beer or ale containing such a bittering agent.

According to yet another aspect of the present invention there is provided a process of preparing a fermented malt beverage such as beer or ale which process consists of adding such a bittering agent to said beverage.

The soft resins and oils, which are contained in the glands produced on the hops and known as lupulin glands, are valuable constituents of the hops as used in the brewing process. The soft resins consist principally of (a) the alpha acids, (b) the beta acids, and (c) the uncharacterized soft resins. The alpha acids are known as humulones and the beta acids are known as lupulones. The alpha acids are the source of antiseptic and bitter substances in beer. The beta acids, or lupulones have low solubility in kettle wort and beer, thus do not appreciably enter into the brewing process.

It is known that chemical changes are made in the humulones during brewing resulting in the compounds known as isohumulones, i.e. isohumulone, isocohumulone, isoadhumulone, and isoprehumulone. These isocompounds are formed in the kettle during the boiling stage of the brewing process, and we have discovered that these compounds are the ones that cause the beer to become sensitive to light in the presence of sulphhydryl compounds.

During the brewing process, the hops are added to the wort and boiled with it. As a result, the extracted humulone fraction, consisting of humulone, adhumulone, cohumulone, and prehumulone, is isomerized to the corresponding isohumulones. It is known that during the isomerization of the humulones to isohumulones, a new side chain is formed which now contains a carbonyl group. It is these isohumulones—iso-humulone, isocohumulone, isoadhumulone, and isoprehumulone—which we have found to be involved in the photochemical reaction with sulphhydryl compounds to produce the actinic insult resulting in the characteristic light struck aroma.

We are of the belief that when the isohumulones are exposed to light, a photochemical reaction takes place involving the cleavage of this side chain from the ring structure forming free radicals. These free radicals

derived from the side chain in turn react with sulphhydryl groups to form an odiferous compound or compounds.

We also believe that the functional portion of the isomers entering into the light reaction is the carbonyl group of the isohexenoyl side chain. This reactive carbonyl group can be altered by means of reduction, for example, to a secondary alcohol, and by such alteration, be prevented from reacting with the sulphhydryl groups normally present in beer components. Various reducing agents can be used, metal borohydrides being particularly suitable.

In practising our invention, one method is to prepare pure humulones. The pure humulones are isomerized to their respective iso derivatives, and subsequently reduced through the addition of sodium borohydride or potassium borohydride (Example 1). Subsequent research has shown that by proper adjustment of temperature concentration and pH value, the purified humulones can be isomerized and reduced in one combined step (Example 2).

For a more practical approach, investigation of the whole hops indicated that they could be extracted, isomerized and reduced similarly to the pure humulones (Example 3). Investigation has shown that the lupulone fraction when exposed to light in the presence of —SH groups can produce a mercaptanous odor. It is our belief that traces of lupulone under specific conditions could be soluble in kettle wort and beer. A method for the removal of this lupulone fraction through a preliminary extraction of an isomerized and reduced hop extract was accomplished (Example 4).

Once again it was desired to investigate the practice of combined isomerization and reduction of a hop extract, resulting in the procedure of Example 5.

Utilizing the technique of a combined isomerization and reduction method and then removing the lupulone fraction has also resulted in a practical and desired procedure (Example 6).

The techniques used in the above examples have also been found to be applicable to fresh hops (Example 7).

The following seven examples illustrate satisfactory procedures for carrying out the invention, but it will be understood that they are presented purely for purposes of illustration and not as indicating the limits of the invention, e.g. temperature, solvent, type of reducing agent, pH, concentration of the components.

The various examples will now be more clearly understood when considered with the accompanying drawing in which:—

Fig. 1 is a graphical presentation illustrating a comparison of ultraviolet absorption curves in alkaline methanol of isohumulones in an unreduced state with a typical curve of

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reduced isohumulones prepared in accordance with certain steps of Example 1; and

Fig. 2 is a graphical presentation similar to Fig. 1 of typical ultraviolet absorption curves is iso-octane extracts of various comparative beers in alkaline methanol, and in accordance with practices outlined in Examples 1 and 3.

EXAMPLE 1.

ISOMERIZATION OF PURIFIED HUMULONE AND REDUCTION OF THE ISOHUMULONE.

200 grams of ground, dried hops are packed in a tube and extracted with 3 liters of low boiling petroleum ether (Skellysolve F). The petroleum ether is evaporated *in vacuo* and the oily residue is taken up in a minimum amount of absolute methanol. The hop waxes which precipitate upon chilling the methanol extract in an ice bath are filtered off and washed with cold methanol. The diluted filtrate is heated to 60° C. and the humulones are precipitated as a lead complex by the addition of 10% methanolic lead acetate solution until precipitation is complete. The lead humulate is digested at 60° C. for 30 minutes, cooled to room temperature and centrifuged. The residue is washed three times by slurring with small amounts of methanol.

The humulones are freed from their lead complex by slurring the lead humulate in 90% methanol and adding 1M (molar solution) H_2SO_4 in methanol with agitation until all of the lead humulate has been dissociated and precipitation of lead sulfate is complete. The insoluble lead sulfate is removed by centrifugation. An equal volume of 2% H_2SO_4 is now added to the lead-free solution of humulones whereupon the humulones become insoluble and are recovered by extracting three times with petroleum ether. The petroleum ether is evaporated *in vacuo* and the humulones may be taken up in a suitable solvent and used in the reduction process such as described below, or they may be first further purified by repeating the precipitation of lead humulate and the subsequent recovery of humulones therefrom.

A solution of 2.43 grams of re-purified humulones in 28 ml. of ethanol in a 500 ml. flask is treated with 7.3 ml. (N) (normal solution)* sodium hydroxide to neutralize the acidity of the humulones. Sufficient 0.2 M phosphate buffer and water are added to make a final volume of 243 ml. containing 1% humulones at pH 11. The phosphate buffer consists of a mixture of 0.2 M disodium hydrogen phosphate and 0.2 M sodium dihydrogen phosphate which yield a buffer solution of pH 11. The contents of the flask are heated to

boiling under reflux for 45 minutes during which time the humulones are converted to isohumulones as evidenced by the typical spectrophotometric curve of isohumulones in the ultraviolet region as illustrated in Fig. 1 of the drawing. The reaction flask and its contents are cooled to room temperature.

The chemical reduction of the isohumulones is accomplished by adding 700 mg. KBH_4 to 230 ml. of the isohumulone solution and stirring at room temperature for 4 hours. At this point the excess borohydride is decomposed by acidification with 6N hydrochloric acid to pH 2 and the reduced isohumulones are recovered by extraction with petroleum ether. The boric acid remains in the aqueous solution. The petroleum ether is removed *in vacuo* leaving a bitter product which is light stable when tested in the presence of sulfhydryl-containing compounds. The spectrophotometric curve of Fig. 1 illustrates the ultraviolet absorption in alkaline methanol to provide the typical plateau of reduced isohumulones exhibited between approximately 260 to approximately 275 millimicrons wave length range. In contrast, isohumulones which have not been reduced exhibit a spectrophotometric curve of gradual descent in the same range.

The reduced isohumulones are taken up in 100 ml. of ethanol and 76.5 ml. of the ethanolic solution containing 1.25 grams of reduced isohumulones is added to 23 liters of unhopped (not containing hops) wort. The wort thus treated is boiled and cooled. Yeast is added and the liquid is fermented. The resulting beer is processed by the usual procedures known to the art. The beer has good foam and taste characteristics.

When the beer in a clear glass bottle is exposed for two hours in a light box containing two daylight-type fluorescent lights and two ultraviolet black lights at a distance of several inches, the beer did not have a skunky aroma. A regularly hopped production beer exposed to light under the same conditions did become light-struck (skunky).

A comparative spectrophotometric analysis of finished beers is illustrated in the curves of Fig. 2, which exhibit a typical non-reduced isohumulone curve of gradual descent in the approximate 260—275 millimicrons wave length range. This contrasts with the typical plateau exhibited by a beer produced by using the reduced isohumulones of Example 1. In order to obtain these curves from regularly hopped, commercially available beers, an initial extraction was made with iso-octane, an aliquot of which was diluted with alkaline methanol.

EXAMPLE 2.

COMBINED ISOMERIZATION OF PURIFIED HUMULONE AND REDUCTION OF ISOHUMULONE.

A solution of 0.88 grams of re-purified humulones in 17 ml. of ethanol is neutralized

* A normal solution is made by dissolving the gram-equivalent weight of substance in sufficient distilled water to make a liter of solution.

with 2.7 ml. of 1N sodium hydroxide and mixed with 80 ml. of 0.125 N sodium hydroxide containing 300 mg. of potassium borohydride. The alkaline solution is held at 60° C. for 1 hour during which time the humulones isomerize to their respective isohumulones which concomitantly are acted upon by the borohydrides to form the reduced isohumulones. The contents of the reaction flask are now cooled to room temperature whereupon the excess borohydride is decomposed by addition of 6N hydrochloric acid, decreasing the pH of the alkaline solution from 12.6 to 2. The reduced isohumulones which separate are recovered by extraction with petroleum ether (Skellysolve F). The solvent is evaporated *in vacuo* and the bitter residue is taken up in ethanol. The ethanolic extract of the reduced isohumulones can now be used in the production of a light stable beer.

EXAMPLE 3.

ISOMERIZATION AND SUBSEQUENT REDUCTION OF A HOP EXTRACT.

50 grams of ground, dried hops are extracted in a tube with 1.2 liters of petroleum ether (Skellysolve F). The extract is concentrated under vacuum and the volume adjusted to 250 ml. According to spectrophotometric analysis, 3.05 grams of humulones and 2.15 grams of lupulones are present from the hop extraction. The petroleum ether is evaporated *in vacuo* and the dark, oily residue is taken up with 30 ml. ethanol. The bitter acids contained therein are neutralized with 14.5 ml. 1N NaOH. The solution is buffered at pH 11 with 150 ml. 0.2 M phosphate buffer and diluted to 300 ml. with water. This 1% humulone solution is refluxed 90 minutes to convert the humulones to isohumulones and then cooled. The chemical reduction of the isohumulones is now accomplished by the addition of 874 mg. potassium borohydride and stirring at room temperature for 4 hours. One-half of the solution (150 ml.) is acidified to pH 2 with 6N HCl to decompose the excess borohydride. This acidification causes the reduced isohumulones, the partially altered lupulones and other substances to become insoluble. This mixture is extracted with petroleum ether to recover the reduced isohumulones and other substances soluble in petroleum ether. The boric acid, however, remains in the aqueous solution. After removal of the petroleum ether *in vacuo*, the oily residue is taken up in 100 ml. of ethanol.

The ethanolic solution containing approximately 960 mg. of reduced isohumulone according to spectrophotometric assay is added to 21 liters of unhopped wort from the brewhouse. The wort is boiled and cooled. Yeast is added and the liquid is fermented. The resulting beer is processed by the usual procedures known to the art. The beer possesses all of the usual fine qualities and is

not sensitive to light. The somewhat light-sensitive lupulone fraction of the hop extract which is more resistant to the above chemical reduction has been eliminated through its insolubility in wort and beer.

A beer made in accordance with the present method provided a spectrophotometric ultraviolet absorption curve as illustrated in Fig. 2 and including the characteristic plateau in the approximate 260–275 millimicrons wave length range.

EXAMPLE 4.

REMOVAL OF LUPULONE FRACTION AFTER ISOMERIZATION AND SUBSEQUENT REDUCTION.

The second half of the isomerized and reduced hop extract solution from the chemical reduction process in Example 3 is acidified with 6N HCl to pH 6.5, although we have found adjustment to a pH between 6.0 and 8.5 to be equally effective. This treatment decomposes the excess borohydride and causes the lupulone fraction to become insoluble. The mixture is extracted with petroleum ether (Skellysolve F) which completely removes the partially altered lupulone fraction and leaves most or all of the reduced isohumulones in the aqueous phase. This aqueous phase is now further acidified with 6N HCl to pH 2 and the mixture is extracted with petroleum ether to recover the reduced isohumulones which contribute to the desirable bitter character and foam stability of beer. Again, the boric acid remains in the aqueous phase. After evaporation of the petroleum ether, the reduced isohumulone fraction is taken up in 100 ml. ethanol and assayed spectrophotometrically.

77 ml. of the ethanolic solution containing about 1.05 grams of reduced isohumulone is added to 21 liters of boiling, unhopped wort. The cooled wort is fermented with yeast and the resulting beer, processed in the usual manner, was not sensitive to light, in accordance with the light test set forth in Example 1.

EXAMPLE 5.

COMBINED ISOMERIZATION AND REDUCTION OF A HOP EXTRACT.

150 grams of ground, dried hops are extracted in a tube by passing 2 liters of petroleum ether (Skellysolve F). The extract is concentrated under vacuum and the volume adjusted to 250 ml. According to spectrophotometric analysis, 8.63 grams of humulones and 6.25 grams of lupulones are present from the hop extraction. A portion of the petroleum ether extract (115 ml.) is evaporated *in vacuo* and taken up in 40 ml. of ethanol. The bitter acids contained therein are neutralized with 19.0 ml. of 1N NaOH and the solution diluted to 100 ml. with water. This solution of hop extract is added to 300

ml. of an alkaline solution of borohydride at 70° C. containing 40 ml. of 1N NaOH and 1.258 grams of potassium borohydride. The resulting mixture which now contains 1% humulone and 0.1N alkalinity is held at 60° C. for 3 hours. During this time the humulones are isomerized to the respective isohumulones which concomitantly are acted upon by the borohydride to form the reduced isohumulones as evidenced by the changes in the spectral curves in the ultraviolet region. The solution is cooled to room temperature.

A 150 ml. portion of the alkaline solution is acidified to pH 2 to decompose the excess borohydride and the reduced isohumulones are recovered by extracting with petroleum ether together with other substances soluble in this solvent. The boric acid remains in the aqueous phase during the extraction. The petroleum ether is evaporated *in vacuo* and the oily, bitter residue is taken up in 100 ml. of ethanol. The ethanolic solution containing 1 gram of reduced isohumulones according to spectrophotometric assay is now added to 22 liters of boiling wort from the brewhouse. The wort is boiled, cooled and fermented with yeast. The resulting beer is processed in the usual manner known to the art and was found to be stable to light.

EXAMPLE 6.

REMOVAL OF LUPULONE FRACTION AFTER COMBINED ISOMERIZATION AND REDUCTION.

Another 150 ml. portion of the hop extract solution from the combined chemical isomerization and reduction process in Example 5 is acidified with 5N HCl to pH 6.4. The excess borohydride is then decomposed and the lupulone fraction becomes insoluble. The mixture is extracted with petroleum ether (Skellysolve F) which completely removes the partially altered lupulone fraction and leaves most or all of the reduced isohumulones in the aqueous phase. This aqueous phase is now further acidified with 5N HCl to pH 2 and the mixture is extracted with petroleum ether which recovers the desirable reduced isohumulone. After evaporation of the solvent, the residue is taken up in 100 ml. ethanol and the ethanolic solution containing about 0.93 gram of reduced isohumulones is added to 21 liters of boiling, unhopped wort. The cooled wort is fermented with yeast, processed in the usual manner, and the resulting beer is not sensitive to light.

EXAMPLE 7.

ISOMERIZATION AND SUBSEQUENT REDUCTION OF EXTRACT FROM FRESH HOPS.

335 grams of fresh, undried hops are packed in a tube and extracted with 4 liters of petroleum ether (Skellysolve F). The solvent is evaporated *in vacuo* and the oily residue taken up in ethanol and filtered to remove insoluble

material. The alcoholic filtrate is brought to 250 ml. with ethanol. According to spectrophotometric assay, 4.75 grams of humulones and 3.45 grams of lupulones have been recovered from the fresh hops. An amount of the hop extract containing 2 grams of humulones in 20 ml. of ethanol is treated with 8.0 ml. of 1N NaOH to neutralize the humulones and lupulones, and further diluted with 100 ml. of 0.2 M phosphate buffer and water to make a final volume of 200 ml. The phosphate buffer in this case is the same as that used in Example 1. The alkaline solution at pH 11 is refluxed for 90 minutes to isomerize the humulones to their respective isohumulones. The solution is cooled, whereupon 596 mg. of potassium borohydride are added and the reaction mixture stirred for 4 hours at room temperature. The excess borohydride is decomposed by the addition of 6N HCl to a pH of 2. The insoluble material containing the desired reduced isohumulones is extracted with petroleum ether. The solvent is evaporated *in vacuo* and the oily residue taken up in 50 ml. of ethanol. A portion of the ethanolic extract containing about 1.0 gram of reduced isohumulones is added to 21 liters of boiling, unhopped wort. The wort is cooled, fermented with yeast and the beer is processed in the usual manner. The beer is stable to light in accordance with the light test set forth in Example 1.

In the practice of our invention, we are not limited to the conditions set forth in the above examples. The chemical reduction of the isohumulones with sodium borohydride or potassium borohydride can be accomplished in non-aqueous solvents such as alcohols, amines and glycol ethers. Lithium aluminum hydride would require anhydrous ethyl ether and other solvents of the ether class. These are but a few of the possible reducing agents and solvents.

The isomerization and reduction of the isohumulones can be carried out over fairly wide pH and temperature ranges, although mildly alkaline conditions and moderate temperatures are preferred. The concentration of the reducing agent can be varied within reasonable limits. Other acids besides hydrochloric acid could be used to reduce the pH and decompose the excess borohydride. Hydrocarbons, chlorinated hydrocarbons, ethers and other solvents which are immiscible with water and will dissolve the product can be used in place of petroleum ether to recover this product.

The concentration of humulone being isomerized to isohumulone which in turn is reduced can be varied considerably. While in the above examples we have used solutions containing 1% humulone, we have also worked with 0.1%, 5% and 10% humulone solutions.

Although it is preferred to add the hop extract directly to the wort as described in Example 1, we have further found that the hop extract obtained in accordance with the



unhopped



present invention may be added at any stage of the usual brewing process to provide an acceptable beer or ale product. It will be apparent that lesser amounts are required if added during steps following the boiling or cooking of the wort.

As previously stated, we have found that the spectral absorption properties of isohumulones, when measured in alkaline methanol, have been changed as a result of the reduction. This change occurs in the ultraviolet region corresponding to about 260 to 275 millimicrons. Fig. 1 illustrates the typical ultraviolet absorption spectra of the isohumulones and the reduced isohumulones described in Example 1 above. The spectral curve of Fig. 1 of the isohumulones resulting from the isomerization of purified humulones exhibits only a slight inflection in the 260 to 275 millimicrons region. However, the spectral curve of Fig. 1 of the reduced isohumulones obtained from the chemical reduction of these same isohumulones has a pronounced flat or plateau portion, which portion may, in some cases, include a second maximum in this same 260 to 275 millimicrons part of the spectrum.

Fig. 2 is illustrative of the typical ultraviolet absorption spectra of isohumulones and reduced isohumulones when measured in alkaline methanol after extraction of beer with iso-octane. The spectral curve of the regularly hopped beer of Fig. 2 results from the iso-octane extraction of a production beer made in the usual manner, wherein whole dried hops are boiled with wort. It is similar to the non-reduced isohumulone curve of Fig. 1 in that it has the typical curvature due to isohumulones which have not been chemically reduced. The remaining comparative curves of Fig. 2 are the spectral absorption curves of the reduced isohumulones recovered by iso-octane extractions of pilot beers from Examples 1 and 3 above. These two curves have the same general form in the 260 to 275 millimicrons region of the ultraviolet spectrum as that for the reduced isohumulones shown by curve 2 of Fig. 1. The optical density data of Figs. 1 and 2 were determined with a "Beckman" (Registered Trade Mark) DK-2 ratio recording spectrophotometer using a 0.012 N alkaline methanol as a reagent blank. Optical density is defined as $\log I_0/I$ wherein I_0 is the light transmission of the reagent and I is the light transmission of the solution tested.

It is quite obvious, therefore, that an iso-octane extract of any beer containing chemically reduced isohumulone as set forth in our invention, and as we have found, will show a significant difference in spectral absorption properties in the 260 to 275 millimicrons region of the electromagnetic spectrum when said iso-octane extract is diluted with alkaline methanol and evaluated spectrophotometrically, as compared to a beer containing isohumulones not so treated.

WHAT WE CLAIM IS:—

1. A process for preparing a bittering agent for a fermented malt beverage such as beer or ale in which process hops are treated to render constituents of the bittering agent, normally chemically reactive with the sulfhydryl groups normally present as a component in such a malt beverage, chemically inactive towards said sulfhydryl groups, so that the bittering agent when combined with the ingredients of said beverage provides a light-stable product free from those chemical effects of actinic attack which would otherwise cause said product to have objectionable light-struck characteristics.

2. A process as claimed in Claim 1, in which the isohumulones normally formed in said hops during the brewing processes are rendered stable to photochemical degradation.

3. A process as claimed in Claim 2, characterised in that photochemical stability of the isohumulones is brought about by reduction.

4. A process as claimed in Claim 3, in which the lupulones normally present in hops are removed whilst retaining the isohumulones in a reduced state.

5. A process as claimed in Claim 4, in which the lupulones are removed subsequent to the formation of the reduced isohumulones.

6. A process as claimed in any of Claims 3 to 5, in which the reduced isohumulones are formed by isomerising, then reducing humulones.

7. A process as claimed in any one of Claims 3 to 5, in which the reduced isohumulones are formed by simultaneously isomerising and reducing humulones.

8. A process as claimed in Claim 6 or 7, in which the humulones are extracted from a hop extract prior to conversion to reduced isohumulones.

9. A process as claimed in Claim 6 or 7, in which the humulones are converted to isohumulones when still constituents of a hop extract.

10. A process as claimed in Claim 8 or 9, in which the hop extract is formed by subjecting hops to the action of a solvent in which the humulones in hops are substantially soluble.

11. A process as claimed in Claim 10, in which said solvent is petroleum ether.

12. A process as claimed in any preceding claim, in which the hops treated are ground dried hops.

13. A process as claimed in any one of Claims 1 to 11, in which the hops are fresh undried hops.

14. A process as claimed in any preceding claim in which the treatment is carried out in such a manner that an iso-octane extract from a fermented beverage containing said bittering agent in alkaline methanol exhibits a spectral ultra-violet absorption curve of optical density plotted against wavelength in millimicrons hav-

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hops of said
inactive
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present invention may be added at any stage of the usual brewing process to provide an acceptable beer or ale product. It will be apparent that lesser amounts are required if added during steps following the boiling or cooking of the wort.

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Fig. 2 is illustrative of the typical ultraviolet absorption spectra of isohumulones and reduced isohumulones when measured in alkaline methanol after extraction of beer with iso-octane. The spectral curve of the regularly hopped beer of Fig. 2 results from the iso-octane extraction of a production beer made in the usual manner, wherein whole dried hops are boiled with wort. It is similar to the non-reduced isohumulone curve of Fig. 1 in that it has the typical curvature due to isohumulones which have not been chemically reduced. The remaining comparative curves of Fig. 2 are the spectral absorption curves of the reduced isohumulones recovered by iso-octane extractions of pilot beers from Examples 1 and 3 above. These two curves have the same general form in the 260 to 275 millimicrons region of the ultraviolet spectrum as that for the reduced isohumulones shown by curve 2 of Fig. 1. The optical density data of Figs. 1 and 2 were determined with a "Beckman" (Registered Trade Mark) DK-2 ratio recording spectrophotometer using a 0.012 N alkaline methanol as a reagent blank. Optical density is defined as $\log I_0/I$ wherein I_0 is the light transmission of the reagent and I is the light transmission of the solution tested.

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WHAT WE CLAIM IS:—

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2. A process as claimed in Claim 1, in which the isohumulones normally formed in said hops during the brewing processes are rendered stable to photochemical degradation.

3. A process as claimed in Claim 2, characterised in that photochemical stability of the isohumulones is brought about by reduction.

4. A process as claimed in Claim 3, in which the lupulones normally present in hops are removed whilst retaining the isohumulones in a reduced state.

5. A process as claimed in Claim 4, in which the lupulones are removed subsequent to the formation of the reduced isohumulones.

6. A process as claimed in any of Claims 3 to 5, in which the reduced isohumulones are formed by isomerising, then reducing humulones.

7. A process as claimed in any one of Claims 3 to 5, in which the reduced isohumulones are formed by simultaneously isomerising and reducing humulones.

8. A process as claimed in Claim 6 or 7, in which the humulones are extracted from a hop extract prior to conversion to reduced isohumulones.

9. A process as claimed in Claim 6 or 7, in which the humulones are converted to isohumulones when still constituents of a hop extract.

10. A process as claimed in Claim 8 or 9, in which the hop extract is formed by subjecting hops to the action of a solvent in which the humulones in hops are substantially soluble.

11. A process as claimed in Claim 10, in which said solvent is petroleum ether.

12. A process as claimed in any preceding claim, in which the hops treated are ground dried hops.

13. A process as claimed in any one of Claims 1 to 11, in which the hops are fresh undried hops.

14. A process as claimed in any preceding claim in which the treatment is carried out in such a manner that an iso-octane extract from a fermented beverage containing said bittering agent in alkaline methanol exhibits a spectral ultra-violet absorption curve of optical density plotted against wavelength in millimicrons hav-

70
1 of which are
in the
sense of
producing
odoriferous
compounds
80

85 incapable
of reacting
to form
odoriferous
compounds
when subjected
to said
inactive
state
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- ing a positive slope portion approaching a maximum optical density value at approximately 250 millimicrons and a generally negative slope following it and including an accentuated intermediate plateau-like curve portion in the approximate wave-length range of 260 to 275 millimicrons.
- 5 15. A process for preparing a bittering agent substantially as herein described with reference to the examples.
- 10 16. A bittering agent for a fermented malt beverage such as beer or ale when prepared by the process claimed in any preceding claim.
- 15 17. A fermented malt beverage such as beer or ale containing a bittering agent as claimed in Claim 16.
18. A process of preparing a fermented malt beverage such as beer or ale, which process consists of adding a bittering agent as claimed in Claim 16 to said beverage.
- 20 19. A process as claimed in Claim 18, in which said bittering agent is added to the beverage during the brewing process.
- 25 20. A process as claimed in Claim 19, in which said bittering agent is added to the wort.
- 30 21. A process of preparing a malt beverage such as beer or ale as claimed in Claim 18 and substantially as herein described.

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