

RESERVE COPY PATENT SPECIFICATION

1,161,787

NO DRAWINGS.

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Date of filing Complete Specification: 15 Nov., 1966.

Date of Application (No. 48866/65): 17 Nov., 1965.

Complete Specification Published: 20 Aug., 1969.

Index at acceptance:—C6 E(11A, H); C2 C(3A12A2, 3A12B5, 3A12C1, XX30Y, XX351, XX353, XX355, XX36Y, XX360, XX363, XX782, XX784).

International Classification:—C 12 c 9/02.

COMPLETE SPECIFICATION.

Manufacture of Hop Extracts.

We, BUSH BOAKE ALLEN LIMITED, a British Company, of Wharf Road, London N.1, 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:—

The present invention relates to the manufacture of hop extracts and to the flavouring of beer therewith.

The term "humulones" is used generically herein to include the α -acids present in hops, e.g. humulone, cohumulone, adhumulone and posthumulones, the isohumulones, such as isohumulone, isocohumulone, isoadhumulone and isoposthumulones and water soluble salts of the aforementioned humulones. "Isohumulones" includes alkali metal isohumulates. " α -acids" includes synthetically prepared humulone, cohumulone, adhumulone and posthumulones. "Fixed oil" refers to the oil contained in the hop seeds which is not extracted by the boiling water in conventional brewing operations. "Essential oil" refers to the relatively volatile oils which contribute to the aroma of hops.

In the traditional brewing process hops are boiled with wort prior to the fermentation step. In the course of this boiling, part of the soft resins (comprising weakly acidic α -acids) is isomerised into a water soluble form and dissolves in the wort. It has long been realised that it is this water soluble isomerised material, comprising isohumulones, which is principally responsible for the bitter flavour of beer. The traditional process has many disadvantages; e.g. it is necessary to store a large bulk of hops which are subject to slow deterioration; it

is difficult to obtain a consistent degree of bitterness; and, in particular, boiling water isomerises only a small proportion of the humulones present in the hops so that much of their potential bitterness is wasted.

A number of attempts have been made to extract the essential flavouring ingredients from hops using organic solvents. One disadvantage of such extracts is that in addition to the humulones and other desirable hop ingredients the organic solvent tends to remove undesirable hop ingredients which can give rise to unpleseant flavours. Moreover the the extracted α -acids upon addition to boiling wort are only partially isomerised.

In order to prepare isohumulones efficiently, it has been proposed to contact the α -acids with hot alkali. The principal disadvantage of this technique is that when hops or solvent hop extracts are contacted with hot alkali, certain other ingredients apart from the humulones undergo degradation giving rise to disagreeable flavours.

Various methods have been proposed for separating the α -acids from the other hop extractives in order to prepare pure isohumulones, but these methods have generally been too costly for commercial application. Moreover pure isohumulones do not impart the full flavour of traditional beer, and their exclusive use results in wastage of other flavour ingredients present in the hops.

In our co-pending Applications Nos. 15363/63, 36382/63 (Serial No. 1,088,631) and 16437/66 (Serial No. 1,142,507), we have described methods by which undesirable flavouring ingredients, such as fixed oils, can be eliminated from the hop ex-

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tract by redissolving in aqueous methanol; and methods by which the α -acids may be isomerised with hot alkali, without generating the usual off-flavours, by dissolving the extract in a water immiscible solvent, partitioning with aqueous alkali and recovering isohumulones from the aqueous phase. However, it has been found that further losses of isohumulones occur when isomerised extracts prepared in this way are added to beer. We have now discovered that this is due to the entrainment of isohumulones in water-insoluble resinous material such as lupulones which are extracted by the alkali and which precipitate in the beer.

We have discovered that it is possible to prepare an extract of hops comprising a high proportion of isohumulones substantially free of lupulones, fixed oils and unpleasant alkali degraded material, if a solution of hop extract in a water-immiscible solvent which dissolves humulate salts less readily than does water is contacted with aqueous alkali at a pH sufficient to transfer the α -acids into the aqueous phase as humulate salts but not sufficient to transfer the lupulones into the aqueous phase as lupulate salts. We have discovered that a humulate or isohumulate salt can conveniently be separated from the aqueous alkaline liquid phase, for example by precipitation using a cation that forms a water-insoluble humulate or isohumulate salt or by solvent extraction with a water-immiscible polar solvent. We have further discovered that the other desirable hop ingredients, including essential oils and lupulones may be conveniently used provided that they are separated from the humulones prior to the isomerisation thereof, freed from any fixed oils and added to the wort as a "kettle additive" prior to the isohumulones.

Our invention provides a method of preparing an isohumulone-containing hop extract which comprises contacting a solution of a solvent extract of hops in a water-immiscible solvent which dissolves humulate salts less readily than does water with an aqueous alkali to form a mixture having a final pH sufficient to transfer the α -acids into the aqueous phase as humulate salts but not sufficient substantially to transfer the lupulones into the aqueous phase as lupulate salts, separating the aqueous phase from the water-immiscible phase, converting the α -acids contained therein, into isohumulates, for example by means of a hot aqueous alkali, and, before or after isomerisation, separating humulate or isohumulate salts, respectively, from a liquid aqueous phase.

Our invention also provides a method of bittering beer which comprises: preparing a bittering additive comprising α -acids substantially free from fixed oils, essential oils and lupulones and a kettle additive com-

prising lupulones and essential oils substantially free from fixed oil; converting the humulones in the bittering additive into isohumulones; adding the kettle additive to wort and subsequently adding the isomerised bittering additive.

Preferably the initial extraction of the hops is carried out on oast dried hops. However, vine fresh or freeze dried hops may also be employed.

A variety of solvents may be used for the extraction including alcohols, ketones, such as acetone, and chlorinated hydrocarbon solvent. We have discovered that benzene is particularly suitable.

In order to carry out the partitioning with aqueous alkali, the solution of crude extract in the extracting solvent may be employed, providing the latter is water immiscible and dissolves alkali metal humulate salts less readily than does water. We have found that the best water immiscible solvents for use in the partitioning step are non-polar hydrocarbons e.g. petroleum ether is especially suitable. If desired the extracting solvent may be evaporated off and the crude extract dissolved in the water immiscible solvent. Alternatively, where a suitable solvent, such as benzene is employed for the extraction, the initial solution of extract may be concentrated by evaporation of part of the extracting solvent and the concentrated solution contacted with the aqueous alkali, using for example, a counter-current extractor.

The aqueous alkali for use in the partitioning step is preferably an aqueous alkali metal or ammonium carbonate (such carbonates are particularly preferred since a bicarbonate is formed, which acts as a buffering agent) especially sodium or potassium carbonate. The alkali should be used in sufficient quantity to provide a final pH which will extract humulones as humulates but not extract the lupulones to any substantial extent as lupulates. The preferred pH of the aqueous phase immediately prior to separation from the organic phase depends on the water-immiscible solvent selected. In the case of petroleum ether the pH may be in the range of 9 to 9.5, to give efficient removal of the humulones but not of any substantial quantity of lupulones. Where benzene is used the pH may be up to 9.8. The alkali should be sufficiently dilute to avoid salting out the humulones, by any bicarbonate formed during extraction. For example a solution of less than 5% w/v carbonate and preferably less than 3% w/v carbonate is suitable, 2.5% to 2% w/v carbonate has been found to give especially good results. If desired the partitioning may be carried out in two or more stages. For example in the first stage the pH of the final mixture may be 9 to 9.2.

The aqueous phase will be separated and the organic phase contacted with portions of alkali at successively higher pH. Each portion of alkali is contacted with successive portions of solution until the pH reaches the desired final level, and is then removed. Alternatively the whole partitioning operation may be performed in a single continuous countercurrent extractor.

A difficulty we have encountered when humulones are separated by a partition technique, where the humulones must be recovered from a dilute aqueous system, is the considerable cost of evaporating the large volume of solvent to recover the extract. Moreover the humulones are liable to deterioration upon prolonged heating. We have discovered that the humulones may be recovered from the aqueous solution as humulate salts by adding thereto the water soluble salt of a metal which forms a water insoluble humulate salt.

The salt used to precipitate the humulones may be any water soluble salt of a cation whose humulate salts are insoluble in the aqueous solution and whose carbonate is preferably insoluble in concentrated aqueous methanol, for example an alkaline earth metal, preferably calcium or magnesium. The anion is not important. For example any water soluble chloride, bromide, iodide, sulphate, nitrate, acetate or similar salt of a metal such as calcium, magnesium, zinc, copper, strontium or nickel may employed. Whether any particular salt is suitable can readily be determined by trial and error.

The precipitated humulate salt may be filtered, dissolved in a suitable organic solvent, e.g. methanol, and converted to an alkali metal humulate by adding the corresponding alkali metal carbonate, whereupon an insoluble metal carbonate precipitates. The former precipitate, comprising insoluble humulate salts, is normally contacted with methanol while still wet (e.g. 97 to 100% w/v methanol) sufficient to give at least 90% w/v methanol in the solution. The alkali metal carbonate, preferably K_2CO_3 , is added in the form of a concentrated aqueous solution. The result is that after removal of the precipitated carbonate (e.g. by filtration) and of the methanol (e.g. by evaporation), there is left a concentrated aqueous solution of the alkali metal salts of the humulones. This solution, after any necessary adjustment of pH and concentration, is boiled to isomerise the humulones. It is also possible to isomerise the humulones prior to the precipitation as an insoluble salt in which case an isohumulate salt is precipitated.

As an alternative to the above described method of converting an insoluble metal humulate or isohumulate into an alkali metal humulate or isohumulate, it is also

possible to employ a suitable cation exchange material (e.g. a cation exchange material of the type sold commercially as Zeo Carb 225), in order to remove the unwanted metal ions from the methanolic solution. The resulting solution may then be neutralised to pH 9 to 10.2, for example with KOH. The methanol is recovered and the neutralised extract is boiled with alkali.

We have discovered that the most effective alkali in the partitioning step is sodium carbonate, but that the isomerisation step is most effectively performed on the potassium humulate. We therefore prefer to contact the water immiscible solution with aqueous sodium carbonate, separate the aqueous phase, recover the humulate salt from the aqueous phase, convert the humulate into a potassium humulate and subsequently isomerise the potassium humulate, for example with aqueous potassium hydroxide or carbonate.

In order to avoid the filtration steps necessary when insoluble humulate salts are precipitated, we have devised an alternative method for separating the humulates or isohumulates from the aqueous solution. According to this alternative we prefer to contact the aqueous solution of alkali metal humulates or isohumulates, after separation from the water immiscible solvent, with a low boiling, polar, water-immiscible solvent, which is sufficiently polar to extract alkali metal humulates from the aqueous solution. Preferably the alkali metal humulates are salted out by addition of a water soluble salt of the alkali metal e.g. where sodium carbonate has been used for the initial partition, NaCl may be employed to salt out the sodium humulates. The preferred water-immiscible polar solvents are low boiling esters such as ethyl or isopropyl acetate, ketones such as methyl isobutyl ketone, and water-immiscible alcohols.

The solution of alkali metal humulates in the water-immiscible polar solvent may be evaporated to recover the humulate. Preferably, however, sodium humulates are prepared initially and then converted to potassium humulates in solution. For example the solution in the polar solvent may be shaken with excess of aqueous mineral acid and washed with water to remove the acid and any residual alkali metal salt used in the salting out operation. The humulones so prepared may be converted to potassium humulates e.g. by addition of aqueous KOH sufficient to bring the pH to about 9. The potassium humulate may be isomerised by first boiling off the water immiscible solvent, adjusting the pH to about 10, and then boiling the remaining aqueous solution.

Humulones, separated from lupulones and essential oils in accordance with this speci-

fication may be isomerised by aqueous alkali. Preferably the pH is in the range 10.0 to 11 (e.g. 10.2). Temperatures above 90°C are preferred e.g. boiling point.

5 The isohumulone containing extract, is preferably added to beer after fermentation.

The hop ingredients remaining in the water-immiscible solvent used in the initial partitioning step or steps, may be recovered after separation from the aqueous phase and freed from any fixed oil and hop waxes by redissolving in aqueous methanol as described in our Application No. 15363/63 (Serial No. 1,088,631). The purified materials comprise lupulones and essential oils, together with soft and hard resins and may be added to the wort. The wort should then be boiled, thereby removing the more volatile fractions of the essential oils leaving only the traces of the less volatile fractions normally present in beer. Alternatively the mixture comprising lupulones and essential oils may be steam-distilled prior to addition to the wort or beer. The lupulone-containing extract should be added in any case prior to the isohumulone-containing extract.

If desired the kettle additive may comprise or be used in conjunction with other hop ingredients such as the water soluble materials which are normally present in beer e.g. tannins and soluble proteins. The extracts according to our invention may be used in conjunction with ordinary hops.

35 Any fixed oil may, if desired, be removed from the initial extract prior to the step of dissolving in the water-immiscible solvent used in the initial partition with aqueous alkali, for example by mixing with sufficient 80 to 95% aqueous methanol to dissolve a part of said kettle additive, separating the methanol from the undissolved material and recovering the dissolved material as described in the aforesaid Application 45 No. 15363/65 (Serial No. 1,088,631). If desired the lupulones may be converted to hulupones by appropriate chemical treatment e.g. alkaline oxidation.

The invention will now be described in more detail in the following examples:—

EXAMPLE I

Ground dried hops were extracted with light petroleum ether (B.P. 75 to 95°C) at a temperature of 30°C. Most of the solvent was removed from the extract by distillation and a concentrate containing approximately 20% weight by volume total solids in the petroleum ether was carried forward to the next stage. This solution was agitated vigorously with a dilute solution (2.5% w/v) of potassium carbonate in water, the addition of this latter solution being continued gradually until the pH of the aqueous phase reached 9.0 to 9.2 The

mixture was allowed to settle and the aqueous layer run off and reserved. The petroleum ether solution was then agitated with further potassium carbonate solution, progressively added until the pH reached a value of 10.0 to 10.2, the mixture was allowed to settle, and the lower layer was then run off. This secondary solution contained a small quantity of the desired humulones, not removed by the first treatment, but in addition it contained some lupulones. It was used as the first part of the solution required to extract the humulones from a further quantity of petroleum ether solution of hop extract, when the lupulones were removed from it by the petroleum ether; further potassium carbonate solution was then gradually added to raise the pH value to 9.0 to 9.1. The initial aqueous solution (pH 9.0 to 9.2) from the first and subsequent batches of hop extract was washed with clean petroleum ether, to remove any remaining unwanted material, and then treated with a 50% w/v aqueous solution of calcium chloride in distinct excess, to precipitate the calcium salts of the desired hop acids. The calcium salts of the humulones were collected by vacuum filtration or by means of a centrifuge, and, while still moist, were dissolved in methyl alcohol. The insoluble solid, consisting of calcium carbonate and bicarbonate was not removed at this stage. Potassium carbonate (50% w/v in water) was added to the methanolic solution until a pH value of 12.0 to 12.2 was obtained; this caused the complete precipitation of the calcium ions in the form of calcium carbonate and/or bicarbonate, the humulones being converted to their soluble potassium salts. The insoluble calcium carbonate and bicarbonate were removed by filtration, the filtrate was adjusted to pH 9.8 to 10.2 with citric acid and the methanol removed from it by distillation under partial vacuum. The residual aqueous solution of the potassium salts of the humulones was diluted with more water to produce a tractable solution containing 30% w/v total solids, boiled for approximately 45 minutes to effect isomerisation; then concentrated by vacuum distillation to a soft extract, containing 10 to 20% of water. The soft extract could be dried under vacuum to a dry product which could be powdered. Products obtained in accordance with the above procedure contained from 40 to 60% of isohumulones, and were suitable for addition to unhopped or lightly hopped beer after fermentation.

The petroleum ether solution from which the humulones had been extracted, was subjected to distillation to recover the solvent. The resultant extract which contained lupulones and other hop resins, and hop essential oil, in addition to undesirable hop

seed oil and other constituents, was then purified with 85% aqueous methyl alcohol as described in our Specification No. 15363/63 and 36382/63 (Serial No. 1,088,631), and was found suitable for use as a "kettle additive" in the production of beer enabling desirable constituents, including the essential oil of hops and lupulones to be utilised to the best advantage.

ing dried hops with benzene and containing 27.4% humulones (by conductimetry); was dissolved in petroleum ether (B.P. 75—95°C; 50 gallons). The insoluble matter was discarded and the solution divided into three equal parts by volume (22 gallons each). Each portion was extracted with 2% w/v aqueous sodium carbonate solution at 40°C in counter current fashion to pH 9.0—9.1 as indicated in the following table:—

EXAMPLE 2

Hop extract (150 lb.) obtained by extract-

	Petrol Solution 1	Petrol Solution 2	Petrol Solution 3
1st. Extraction	Add 40 gallons alkali pH 9.15	Add aqueous phase from 2nd. extraction of Solution 1 + 5 gallons alkali (pH 9.05)	Add aqueous phase from 2nd. extraction of Solution 2 + 5 gallons alkali (pH 9.05)
2nd. Extraction	Organic Phase Add 40 gallons alkali (pH 10.3)	Organic Phase Add aqueous phase from 3rd. extraction of Solution 1 (pH 10.15)	Organic Phase Add aqueous phase from 3rd. extraction of Solution 2 (pH 10.2)
3rd. Extraction	Organic Phase Add 40 gallons alkali (pH 10.5)	Organic Phase Add 40 gallons alkali (pH 10.4)	

The three aqueous solutions at pH 9.15 and 9.05 were bulked and washed with petroleum ether (B.P. 75—95°C; 50 gallons).

The resultant washed aqueous solution (total volume 130 gallons) was treated with a saturated aqueous solution of sodium chloride (15 gallons) and extracted with three portions of ethyl acetate (each of 15 gallons). The resultant ethyl acetate solutions were combined and treated with 10% w/v aqueous hydrochloric acid (10 gallons). After thorough agitation the mixture was allowed to separate and the lower aqueous phase run off and discarded. The ethyl acetate solution was treated with 10% w/v aqueous potassium hydroxide (q.s.), by gradual addition with stirring until the pH of the aqueous phase reached 9.0. The lower aqueous layer was run off and reserved. The solvent was removed from the ethyl acetate solution by distillation and the reserved aqueous layer added to the residue. The pH of the aqueous solution was adjusted to a value of 10.0 by the addition of 25% w/v aqueous potassium carbonate (q.s.) and the mixture boiled at

atmospheric pressure for 90 minutes, to achieve isomerisation.

The isomerised solution was then evaporated under vacuum, to give the required product (62.1 lb.), as a soft extract containing 48.8% isohumulones (by counter current analysis) and 20% residual water.

Therefore the conversion recovery of isohumulones from the starting material was 73.6% of theory.

EXAMPLE 3

Hop extract (146 lb.) obtained by extracting dried hops with benzene and containing 26.9% humulones was dissolved in petroleum ether (B.P. 75—95; 74 gallons) and the insoluble matter reserved. The resultant solution was agitated vigorously with 2% aqueous sodium carbonate solution (180 gallons total) added in 10 gallon quantities after an initial quantity of 150 gallons, until the pH of the aqueous phase reached a value of 9.1, the aqueous layer was run off and washed with clean petroleum ether (B.P. 75—95; 50 gallons). The washed aqueous solution was

reserved and the relatively clean petrol layer was used together with a further quantity (20 gallons) of clean petrol to dissolve a further quantity (141 lb.) of hop extract.

- 5 The initial petroleum solution, from which the greater part of humulones had been extracted, was further extracted with 2% w/v aqueous carbonate solution (150 gallons) to a resultant pH of 10.2. This solution
10 was used as the first extracting solution for the second quantity of hop extract already dissolved in petroleum ether, the volume (152 gallons) being sufficient to achieve a pH value of 9.1 after agitation. The
15 aqueous solution was run off and washed with clean petroleum ether (B.P. 75—95°C; 50 gallons) then reserved for further treatment.

- The two reserved aqueous solutions (pH 9.1) were treated with 25% aqueous solution of calcium chloride (18 gallons) and the resultant precipitate of calcium salts collected on a vacuum filter. Without drying, the precipitate was dissolved in absolute methanol (180 gallons) and the resultant
25 solution treated with 50% w/v aqueous potassium carbonate (11 1/2 gallons) to give a pH value of 12.0. The precipitated calcium carbonate was removed by filtration and the pH of the filtrate reduced to
30 a value of 9.0 by the addition of 25% w/v aqueous citric acid solution (6 pints). The methanol was then recovered by distillation under vacuum. To the residue was added
35 sufficient distilled water to give a total volume of 55 gallons and sufficient 50% w/v aqueous potassium carbonate (10 pints) added to give a pH value of 10.1. The solution was then boiled at atmospheric
40 pressure for 50 minutes to achieve isomerisation and then concentrated under vacuum until the concentrate weighed 180 lb. After standing for 24 hours this material separated into two layers, the lower brown
45 viscous layer, being the desired product weighed 144 1/2 lb. and contained 36.6% isohumulones and 18% of water.

- The recovery, therefore, of isohumulones from the humulones present in the original
50 hop extract (287 lb. at 26.9% humulones) was 69% of theory.

- The residual petroleum ether solutions were distilled to recover the solvent and the residue together with the reserved
55 petrol insoluble residue was purified by treatment with 90% w/v methanol, to reject unwanted hop seed oil and other material. By recovering the methanol a kettle
60 additive (90 lb.) rich in lupulones and essential oil of hops was obtained.

EXAMPLE 4

Hop extract (40 lb.) obtained by extracting oast hops with benzene and containing 32.4% humulones (by conductivity), was

dissolved in 20 gallons of benzene. This
benzene solution was countercurrent extracted with 2% aqueous sodium carbonate solution at a temperature of 40°C in a 'Rotating Disc Contactor'. The relative
rate of flow of the aqueous carbonate to
benzene solutions was 20 gallons/hour to
10 gallons/hour at steady state conditions. The aqueous carbonate solution from the
contactor (55 gallons) at a pH 9.7 was collected and filtered to remove entrained material. The clear filtrate was reheated to
40°C and treated with 20 lb. of CaCl₂ · 6H₂O dissolved in 5 gallons of water. The precipitated calcium salts were obtained by
filtering off the aqueous solution in a basket
centrifuge. The calcium humulates were
dissolved in 10 gallons of warm (40°C)
methanol and 25% w/v aqueous potassium carbonate (2.5 gallons) was added to raise
the pH of 12.0. The resulting precipitate
was removed by filtration and the clear
filtrate was back adjusted to pH 9.0 with
saturated citric acid solution (70 ml.) and
the methanol recovered under vacuum at a
temperature of 40°C. The potassium
humulone concentrate after methanol recovery was dissolved in 5 gallons of distilled water, the pH was adjusted to 10.0
with 25% w/v aqueous potassium carbonate
solution and the humulones were isomerised
to isohumulones by boiling at atmospheric
pressure for 1.5 hours. On completion, the
solution was rapidly evaporated under
vacuum to yield 20 lb. of a soft extract.
The product contained 50% isohumulones;
10 giving a recovery of 77.2% from the humulones contained in the original hop extract.

The extracted benzene solution, now free of humulones, was distilled to recover the
benzene. The residue (25 lb.) was freed from hop seed oil and other undesirable constituents by dissolution in 90% w/v methanol, rejecting the insoluble material and recovering the methanol, to give a kettle
additive (12 lb.) rich in lupulones and hop essential oil.

WHAT WE CLAIM IS:—

1. Method of preparing an isohumulone-containing hop extract which comprises contacting a solution of a solvent extract of hops in a water-immiscible solvent, which dissolves alkali metal humulate salts less readily than does water, with an aqueous alkali, the final mixture having a pH sufficient to transfer the α -acids into the aqueous phase as humulate salts but not sufficient substantially to transfer the lupulones into the aqueous phase as lupulate salts, separating the aqueous phase containing the humulate salts, subsequently isomerising the humulate salts, and, before or after isomerisation, separating humulate or iso-

reserved and the relatively clean petrol layer was used together with a further quantity (20 gallons) of clean petrol to dissolve a further quantity (141 lb.) of hop extract.

- 5 The initial petroleum solution, from which the greater part of humulones had been extracted, was further extracted with 2% w/v aqueous carbonate solution (150 gallons) to a resultant pH of 10.2. This solution
10 was used as the first extracting solution for the second quantity of hop extract already dissolved in petroleum ether, the volume (152 gallons) being sufficient to achieve a pH value of 9.1 after agitation. The
15 aqueous solution was run off and washed with clean petroleum ether (B.P. 75—95°C; 50 gallons), then reserved for further treatment.

- The two reserved aqueous solutions (pH 9.1) were treated with 25% aqueous solution of calcium chloride (18 gallons) and the resultant precipitate of calcium salts collected on a vacuum filter. Without drying, the precipitate was dissolved in absolute
25 methanol (180 gallons) and the resultant solution treated with 50% w/v aqueous potassium carbonate (11 1/2 gallons) to give a pH value of 12.0. The precipitated calcium carbonate was removed by filtration and the pH of the filtrate reduced to
30 a value of 9.0 by the addition of 25% w/v aqueous citric acid solution (6 pints). The methanol was then recovered by distillation under vacuum. To the residue was added
35 sufficient distilled water to give a total volume of 55 gallons and sufficient 50% w/v aqueous potassium carbonate (10 pints) added to give a pH value of 10.1. The solution was then boiled at atmospheric
40 pressure for 50 minutes to achieve isomerisation and then concentrated under vacuum until the concentrate weighed 180 lb. After standing for 24 hours this material separated into two layers, the lower brown
45 viscous layer, being the desired product weighed 144 1/2 lb. and contained 36.6% isohumulones and 18% of water.

- The recovery, therefore, of isohumulones from the humulones present in the original
50 hop extract (287 lb. at 26.9% humulones) was 69% of theory.

- The residual petroleum ether solutions were distilled to recover the solvent and the residue together with the reserved
55 petrol insoluble residue was purified by treatment with 90% w/v methanol, to reject unwanted hop seed oil and other material. By recovering the methanol a kettle
60 additive (90 lb.) rich in lupulones and essential oil of hops was obtained.

EXAMPLE 4

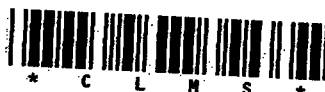
Hop extract (40 lb.) obtained by extracting oast hops with benzene and containing 32.4% humulones (by conductivity), was

dissolved in 20 gallons of benzene. This
65 benzene solution was countercurrent extracted with 2% aqueous sodium carbonate solution at a temperature of 40°C in a 'Rotating Disc Contactor'. The relative
70 rate of flow of the aqueous carbonate to benzene solutions was 20 gallons/hour to 10 gallons/hour at steady state conditions. The aqueous carbonate solution from the
75 contactor (55 gallons) at a pH 9.7 was collected and filtered to remove entrained material. The clear filtrate was reheated to 40°C and treated with 20 lb. of CaCl₂ 6H₂O dissolved in 5 gallons of water. The precipitated calcium salts were obtained by
80 filtering off the aqueous solution in a basket centrifuge. The calcium humulates were dissolved in 10 gallons of warm (40°C) methanol and 25% w/v aqueous potassium carbonate (2.5 gallons) was added to raise
85 the pH of 12.0. The resulting precipitate was removed by filtration and the clear filtrate was back adjusted to pH 9.0 with saturated citric acid solution (70 ml.) and the methanol recovered under vacuum at a
90 temperature of 40°C. The potassium humulone concentrate, after methanol recovery was dissolved in 5 gallons of distilled water, the pH was adjusted to 10.0 with 25% w/v aqueous potassium carbonate solution and the humulones were isomerised
95 to isohumulones by boiling at atmospheric pressure for 1.5 hours. On completion, the solution was rapidly evaporated under vacuum to yield 20 lb. of a soft extract. The product contained 50% isohumulones; 100 giving a recovery of 77.2% from the humulones contained in the original hop extract.

The extracted benzene solution, now free of humulones, was distilled to recover the
105 benzene. The residue (25 lb.) was freed from hop seed oil and other undesirable constituents by dissolution in 90% w/v methanol, rejecting the insoluble material and recovering the methanol, to give a kettle
110 additive (12 lb.) rich in lupulones and hop essential oil.

WHAT WE CLAIM IS:—

1. Method of preparing an isohumulone-containing hop extract which comprises contacting a solution of a solvent extract of
115 hops in a water-immiscible solvent, which dissolves alkali metal humulate salts less readily than does water, with an aqueous alkali, the final mixture having a pH sufficient to transfer the α -acids into the aqueous
120 phase as humulate salts but not sufficient substantially to transfer the lupulones into the aqueous phase as lupulate salts, separating the aqueous phase containing the
125 humulate salts, subsequently isomerising the humulate salts, and, before or after isomerisation, separating humulate or iso-



humulate salts respectively from a liquid aqueous phase.

2. Method according to claim 1 wherein the water-immiscible solvent is a non-polar solvent.

3. Method according to either of claims 1 or 2 wherein the aqueous alkali is an alkali metal or ammonium carbonate.

4. Method according to claim 3 wherein the aqueous alkali is aqueous sodium or potassium carbonate.

5. Method according to either of claims 3 or 4 wherein the concentration of the carbonate solution is less than 5% w/v.

6. Method according to claim 5 wherein the concentration of the carbonate is less than 3% w/v.

7. Method according to any foregoing claim wherein the humulate salts are isomerised by hot aqueous alkali.

8. Method according to claim 7 wherein the said hot aqueous alkali is sodium or potassium carbonate.

9. Method according to any foregoing claim wherein the solvent extract of hops is prepared employing benzene as the extracting solvent.

10. Method according to any foregoing claim wherein the water-immiscible solvent is petroleum ether.

11. Method according to any foregoing claim wherein the water-immiscible solvent is the same as the extracting solvent.

12. Method according to any foregoing claim wherein a water soluble salt of a cation which forms a water soluble humulate, is added to the aqueous phase, and the precipitated humulate or isohumulate is separated.

13. Method according to claim 12 wherein the cation is calcium or magnesium.

14. Means according to either of claims 12 and 13 wherein the insoluble humulate or isohumulate is dissolved in an organic solvent in which the carbonate of the metal cation is insoluble, and an alkali metal carbonate is added thereto.

15. Method according to claim 14 wherein the metal cation has a carbonate which is insoluble in methanol, the organic solvent is methanol and the final solution contains up to 10% by volume of water.

16. Method according to any foregoing claim wherein an aqueous phase containing humulates or isohumulates is contacted with a water-immiscible solvent which is sufficiently polar to extract alkali metal humulates or isohumulates from the aqueous phase.

17. Method according to claim 16 wherein the water-immiscible polar solvent is a low boiling ester, alcohol or ketone.

18. Method according to any foregoing claim wherein the water-immiscible polar

solvent is ethyl acetate, isopropyl acetate or methyl isobutyl ketone.

19. Method according to any of claims 16 to 18 wherein a water soluble salt having the same alkali metal cation as the humulate or isohumulate is added to the aqueous phase.

20. Method according to any of claims 16 to 19 wherein the water-immiscible polar solvent is contacted with excess aqueous acid after separation from the aqueous alkaline phase.

21. Method according to claim 20 wherein the acidified solution is contacted with potassium hydroxide.

22. Method according to claim 21 wherein potassium humulates prepared according to that claim are recovered by evaporation of the water-immiscible polar solvent and isomerised by contacting with hot aqueous potassium hydroxide or carbonate.

23. The method of bittering beer which comprises:

preparing a bittering additive comprising α -acids substantially free of fixed oils, essential oils and lupulones, and a kettle additive comprising lupulones and essential oils substantially free of fixed oils; converting the α -acids in the bittering additive into isohumulones; adding the kettle additive to wort and subsequently adding the isomerised bittering additive.

24. Method according to claim 23 wherein the kettle additive comprises essential oils, lupulones and hard and soft resins, but is substantially free of humulones and fixed oils.

25. Method according to either of claims 23 and 24 wherein the kettle additive is added to the wort prior to the boiling thereof and the bittering additive is added after fermentation.

26. Method according to any of claims 23 to 25 wherein the additives are obtained by preparing an organic solvent extract of hops; contacting a solution of the solvent extract in a water immiscible solvent which dissolves humulate salts less readily than does water with an aqueous alkali to form a mixture having a final pH sufficient to transfer the α -acids into the aqueous phase as humulates but not to transfer the lupulones into the aqueous phase as lupulones; separating the aqueous phase, and recovering the said bittering additive therefrom; recovering the said kettle additive from the water immiscible phase; and separating the kettle additive from any fixed oil.

27. Method according to claim 26 which comprises the steps of any claims 2-20.

28. Method according to either of claims 26 or 27 wherein the kettle additive is separated from fixed oils by redissolving in sufficient 80-95% aqueous methanol to dis-



solve a part of the said kettle additive, separating the methanol solution from the undissolved material and recovering the dissolved material.

5 29. Method according to claim 1 substantially as described herein with reference to any of the examples.

30. Isohumulone-containing hop extracts prepared in accordance with any of the
10 foregoing claims.

31. Kettle additives prepared by the

method of any of claims 26—28.

32. Beer containing a hop extract according to claim 30.

33. Beer prepared according to any of 15 claims 23 to 28.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1969,
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.

PATENTS ACT, 1949

SPECIFICATION NO. 1,161,787

The following corrections were allowed under Section 78 on 5th November 1969

Page 7, line 36, for "soluble" read "insoluble"

THE PATENT OFFICE,
1st December 1969

D 120245/18

ERRATUM

SPECIFICATION NO. 1,161,787

SLIP 2

Page 1, for Index at Acceptance C2C only read:-

(3A12A2, 3A12B5, 3A12C1, 30Y, 351, 353, 355, 36Y, 360, 363, 782, 784, XX)

THE PATENT OFFICE,
25th February 1970

D 122572/28

