

PATENT SPECIFICATION

(11) 1 567 634

1 567 634

- (21) Application No. 43034/76 (22) Filed 15 Oct. 1976
(31) Convention Application No. 4640/75
(32) Filed 15 Oct. 1975 in
(33) Denmark (DK)
(44) Complete Specification published 21 May 1980
(51) INT CL³ C12C 11/04 7/00/C12H 1/00
(52) Index at acceptance
C6E FBB



(54) A METHOD OF BREWING BEER OF IMPROVED STABILITY

(71) We, DE FORENEDE BRYGGERIER A/S, a Danish Company, of Vesterfaelledvej 100, DK-1799 Copenhagen V, Denmark, 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 a method of brewing beer having an improved haze stability and shelf life by the use of a wort of barley or malted barley and fermenting the wort.

In the brewing of beer barley is malted, the malt alone or together with carbohydrate adjuvants mashed to give wort and the wort fermented with yeast to give beer. The beer is then stored. This results in products which have a limited stability or shelf life. After filling bottles and casks and pasteurizing, the beer becomes hazy when left to stand for some time. Dependent upon the type of beer, the storage time and the temperature of storage, different degrees of haze, from a faintly blurred appearance to visible fluffs or a precipitate develops. This change in the appearance of the beer is accelerated by high temperatures such as 40—60°C. The so-called colloidal stability of the beer depends upon the length of time the beer stays clear. The higher the colloidal stability the longer it remains clear.

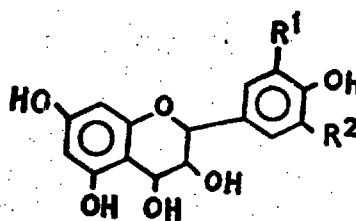
The tendency to haze formation which occurs after bottling the beer is often determined as the so-called chill-haze of the beer when, after storage at temperatures of from 10 to 60°C, it is cooled down to temperatures of about 0°C for 24—48 hours. The amount of chill-haze is used as an index of the chemical or colloidal stability of the beer; the lower the chill-haze the longer the shelf life of the beer.

In the brewing literature an alternative definition of the chill-haze in beer is often used, viz. the difference between the haze of the beer measured at 0°C and the haze of the same beer measured after storage at room temperature for a predetermined period of time. This chill-haze, which increases with the age of the beer after bottling, is a measure of the stability of the beer; the less haze the longer the shelf life of the beer.

This normally occurring haze formation is due to various causes, but the most important factors affecting the haze formation are the contents of oxygen, proteins, polypeptides and polyphenols.

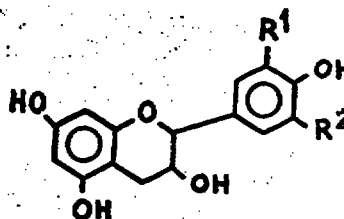
Generally proteins and polypeptides react with flavonoids, a particular class of polyphenols, to form compounds which are insoluble in beer, whilst oxygen will cause oxidation and polymerisation of the polyphenols so that they will develop a greater capacity than the monomeric compounds for reacting to form insoluble compounds with proteins and polypeptides.

It is generally known that the so-called anthocyanogens (3,4-flavanediols), which are a group of the flavonoids, contribute in a marked degree to haze formation, and tests have shown that the stability of beer under otherwise identical conditions is highest in samples drawn from barley having the lowest content of anthocyanogens. Chemically the anthocyanogens are derivatives of the flavanediols (Harris and Ricketts Journal of the Institute of Brewing 1958, 22—32, and European Brewing Convention, Proceedings of the Congress, Rome, 1959, 290—302) who gave them the general formula:—



in which R^1 and R^2 can be either H, OH or OCH_3 .

Another group of flavanoids which also participate in the haze formation of beer is the catechins. However, their effect is not considered to be as decisive as that of the anthocyanogens. The general formula of these compounds is the following:—



in which R^1 and R^2 can be either H, OH or OCH_3 .

Barley normally contains from 120 to 200 mg of anthocyanogens and from 120 to 200 mg of catechins per 100 g of dry barley.

It has been demonstrated in several works appearing in the late sixties that the monomeric anthocyanogens or catechins are incapable of precipitating high-molecular weight proteins and thus form a haze in beer but have first to be polymerized. This also happens in the beer, and the polymerization may occur not only between the same type of molecule but also between anthocyanogen and catechin; the polymerization products formed are described as bi-, tri-, tetra-flavanoids and so on. A biflavanoid has been found in barley and malt. It is also known that the polymerization is accelerated by oxygen.

The introduction by Harris and Ricketts of the term "anthocyanogens" was rapidly accepted in the brewing literature. Freudenberg and Weinges, however, described the same group of substances as "proanthocyanidins" (Tetrahedron, London 1960, volume 8, page 336), and this term has been accepted to some extent in brewery literature in later years.

It is desirable to produce beer with a maximum of stability, i.e. to avoid or delay the normal haze formation. In order to achieve this it has been suggested to exclude atmospheric oxygen during filtering and filling and to separate or remove the substances that cause hazing, particularly the anthocyanogens.

Additives of various types have been used to neutralize or remove the anthocyanogens. Such additives or stabilizers act in one of the following ways (a) they react with oxygen, (b) they absorb polyphenols or proteins, (c) they precipitate polyphenols or proteins and (d) they degrade proteins.

Examples of useful additives of this type include insoluble polyvinylpyrrolidone and silica gel, which adsorb and remove the anthocyanogens wholly or in part and thus increase the stability of the beer. However, complete removal of the anthocyanogens and catechins in this way would require the use of unacceptably large amounts of stabilizers, and the necessary subsequent filtering procedure would be impeded.

Since the content of anthocyanogen and the content of catechin are different with different strains of barley there is the possibility of bringing about improvement in stability by using a strain of barley having as low as possible a content of anthocyanogens and/or catechins as starting material in the production of beer. It has been suggested that by hybridizing available strains of barley it would be possible to obtain strains having a lower content of anthocyanogens and thus to produce beer having a longer shelf life (B. Trolle, Brygmesteren, No. 2, 1960, pp. 45—55). However, this approach has not so far produced any practical results.

By the use of mutating agents barley mutants have been raised that do not synthesize anthocyanogens in leaves, stem and ear (A. Gustafsson, A. Hagberg, U.

Lungqvist and G. Persson, Hereditas volume 62, pages 409—414 (1969); R. A. Nilan, The Cytology and Genetics of Barley 1951—1962, Washington University Press 1964).

5 Anthocyanins and anthocyanidine derivatives are pigments formed during the same flavonoid synthesis as that which leads to the anthocyanogens. The experiments which led to the present invention included detailed examination of a number of anthocyanin-free mutants, only a single one of which, however, was found to be suitable for the brewing of beer of improved haze stability and shelf life.

10 The suitable mutant, identified as ANT-13, was found to be free from anthocyanogens and must thus have acquired an inherent genetic blocking of the anthocyanogen synthesis.

15 The present invention is thus based on the recognition that manufacture of beer having high colloidal stability can only be achieved by using a mutant in which there is a genetic blocking of a step in the common biochemical synthesis which leads to anthocyanogens or proanthocyanidins, while this effect will not be obtained by using other anthocyanin-free mutants in which only that branch of the biochemical synthesis which leads to anthocyanidins is affected.

20 It is the object of the present invention to improve the haze stability of beer produced from barley or malted barley.

25 A further object is to produce beer of improved stability without addition of precipitants or other additives.

30 In accordance with the present invention there is provided a method of brewing beer having an improved haze stability and shelf life by preparing a wort from barley or malted barley and fermenting the wort, characterized in that a barley is used which has a content of anthocyanogens and/or catechins of less than 100 mg per 100 g of dry barley, which content has been brought about by an inherent genetic blocking of the anthocyanogen synthesis and/or catechin synthesis in the barley.

35 The production of beer from a barley having a low content of anthocyanogen and/or catechin may proceed by conventional brewing methods, using conventional yeast or fungi for carrying out the fermentation step.

40 To obtain the desired significant improvement in the haze stability of the beer the barley used in preparing the wort should have a content of anthocyanogens and/or catechins less than 100 mg per 100 g of dry barley. The preferred content of anthocyanogens in the barley used is less than 20 mg per 100 g of dry barley and that of catechins is likewise less than 20 mg per 100 g of dry barley, whilst optimum results are attained using barley having a content of anthocyanogens and catechins each less than 10 mg per 100 g of dry barley. The barley used may be a mutant of the strain Foma.

45 As indicated above, the available strains of barley generally have a content of more than 100 mg of anthocyanogens and more than 100 mg of catechins per 100 g of dry barley, the anthocyanogen content being determined by the method proposed by M. Dacic: ASBC Proceedings 1971, page 159.

50 The invention will be illustrated by the following example, which describes two parallel brewing experiments, one using an anthocyanogen-free and catechin-free mutant identified as ANT-13, of the barley strain having the name Foma and the other with a strain of barley (Ymer) commonly used for brewing of beer. The malt and beer were made from both strains in traditional manner. Analyses were carried out on the barley, the malt, the wort, and the beer obtained. The results were as follows:—

nation of
cisive as
is the
5
from 120
10
that the
ng high-
st to be
ccur not
gen and
i-, tetra-
It is also
15
ens" was
however,
hedron,
e extent
20
avoid or
ested to
remove
25
ove the
ways (a)
cipitate
30
soluble
anogens
omplete
e use of
filtering
35
ifferent
about
ssible a
duction
t would
thus to
60, pp.
esults.
do not
erg, U.
40
45

EXAMPLE		ANT-13	Ymer	
Strain of Barley				
5	Barley: anthocyanogens mg/100 g dry matter	0	140	
	catechins mg/100 g dry matter	1	147	
	Malt: extract, fine-meal %/dry matter (Plato)	79.6	78.6	
	anthocyanogens mg/100 g dry matter	1	110	5
	catechins mg/100 g dry matter	4	130	
10	Wort: original extract % Plato	10.9	10.9	
	attenuation limit apparent %	77.0	77.5	
	anthocyanogens mg/liter	0	73	10
	Beer: original extractor % Plato	10.8	10.7	
	attenuation apparent %	74	74	
15	anthocyanogens mg/liter	1	57	
	head retention, seconds	99	90	
	ml air in head space	0.8	0.8	15
	increase in chill-haze after storage at 45°C			
	1 week EBC-units	0.2	4.4	
	4 weeks EBC-units	0.8	>20	
Methodology of Analysis				
20	Anthocyanogens	M. Dadić: A.S.B.C. Proceedings 1971, 159—170, M. Dadić & N. M. Morrison: A.S.B.C. Proceedings 1972, 50—56. see anthocyanogens		20
25	Catechins	Analytica-EBC, 3rd Ed. E 25.		25
	Extract of malt	Analytica-EBC, 3rd Ed. E 55.		
	Original extract in wort	Analytica-EBC, 3rd Ed. E 58.		
	Apparent attenuation limit of wort	Analytica-EBC, 3rd Ed. E 55.		
	Original extract of beer	Analytica-EBC, 3rd Ed. E 58.		
30	Apparent attenuation of beer	Blom's Method:		30
	Head retention	EBC. Proceedings 1957, 51.		
	Chill-haze in beer	Tuborg Method: Fresh-drawn beer is left to stand for 48 hours at 0°C; haze measured by means of Zeiss* nephelometer, red light, conversion to EBC-units.		35
35		After storage at 45°C for respectively 1 to 4 weeks the chill-haze is deter- mined as above described.		
40		The increase is the difference between the values of the two readings.		40

* The word "Zeiss" is a Registered Trade Mark.

WHAT WE CLAIM IS:—

- 45 1. A method of brewing beer having an improved haze stability and shelf-life
by preparing a wort from barley or malted barley and fermenting the wort,
characterized in that a barley is used which has a content of anthocyanogens and/or
catechins of less than 100 mg per 100 g of dry barley which content has been
brought about by an inherent genetic blocking of the anthocyanogen synthesis
and/or catechin synthesis in the barley.
- 50 2. A method according to Claim 1, in which the content of anthocyanogens
and/or catechins of the barley used is less than 20 mg per 100 g of dry barley.
- 50 3. A method according to Claim 1 or 2 in which the content of anthocyanogens
and/or catechins of the barley used is less than 10 mg per 100 g of dry barley.
- 55 4. A method according to any of the preceding claims in which the barley used
is a mutant of the strain Foma.
- 55 5. A method according to Claim 4 in which the mutant is ANT-13.



13

4

1,567,634

4

EXAMPLE

	Strain of Barley	ANT-13	Ymer
	Barley: anthocyanogens mg/100 g dry matter	0	140
	catechins mg/100 g dry matter	1	147
5	Malt: extract, fine-meal %/dry matter (Plato)	79.6	78.6
	anthocyanogens mg/100 g dry matter	1	110
	catechins mg/100 g dry matter	4	130
	Wort: original extract % Plato	10.9	10.9
	attenuation limit apparent %	77.0	77.5
10	anthocyanogens mg/liter	0	73
	Beer: original extractor % Plato	10.8	10.7
	attenuation apparent %	74	74
	anthocyanogens mg/liter	1	57
	head retention, seconds	99	90
15	ml air in head space	0.8	0.8
	increase in chill-haze after storage at 45°C		
	1 week EBC-units	0.2	4.4
	4 weeks EBC-units	0.8	>20

Methodology of Analysis

20	Anthocyanogens	M. Dadić: A.S.B.C. Proceedings 1971, 159—170, M. Dadić & N. M. Morrison: A.S.B.C. Proceedings 1972, 50—56.
25	Catechins	see anthocyanogens
	Extract of malt	Analytica-EBC, 3rd Ed. E 25.
	Original extract in wort	Analytica-EBC, 3rd Ed. E 55.
	Apparent attenuation limit of wort	Analytica-EBC, 3rd Ed. E 58.
	Original extract of beer	Analytica-EBC, 3rd Ed. E 55.
	Apparent attenuation of beer	Analytica-EBC, 3rd Ed. E 58.
30	Head retention	Blom's Method: EBC. Proceedings 1957, 51.
	Chill-haze in beer	Tuborg Method: Fresh-drawn beer is left to stand for 48 hours at 0°C: haze measured by means of Zeiss* nephelometer, red light, conversion to EBC-units.
35		After storage at 45°C for respectively 1 to 4 weeks the chill-haze is deter- mined as above described.
40		The increase is the difference between the values of the two readings.

* The word "Zeiss" is a Registered Trade Mark.

WHAT WE CLAIM IS:—

1. A method of brewing beer having an improved haze stability and shelf-life by preparing a wort from barley or malted barley and fermenting the wort, characterized in that a barley is used which has a content of anthocyanogens and/or catechins of less than 100 mg per 100 g of dry barley which content has been brought about by an inherent genetic blocking of the anthocyanogen synthesis and/or catechin synthesis in the barley.
2. A method according to Claim 1, in which the content of anthocyanogens and/or catechins of the barley used is less than 20 mg per 100 g of dry barley.
3. A method according to Claim 1 or 2 in which the content of anthocyanogens and/or catechins of the barley used is less than 10 mg per 100 g of dry barley.
4. A method according to any of the preceding claims in which the barley used is a mutant of the strain Foma.
5. A method according to Claim 4 in which the mutant is ANT-13.



14

4

5

1,567,634

5

6. A method of brewing beer of improved stability according to Claim 1 and substantially as hereinbefore described.

7. Beer whenever brewed by the method claimed in any of the preceding claims.

BARON & WARREN,
16, Kensington Square,
London, W8 5HL,
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

Ymer

140

147

78.6

110

130

10.9

77.5

73

10.7

74

57

90

0.8

4.4

>20

5

10

15

20

25

30

35

40

45

50

55

9—170,

—56.

d for
l by
red

ctively
ter-

etween

shelf-life
ne wort,
as and/or
has been
synthesis

anogens
barley.

anogens
barley.
ley used