

PATENT SPECIFICATION

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(54) PROCESS FOR THE DECAFFEINATION OF COFFEE

(71) We, STUDIENGESELLSCHAFT KOHLE mbH of 1 Kaiser-Wilhelm-Platz, 433 Mülheim/Ruhr, Germany a body corporate organised under the laws of Germany, 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 process for the decaffeination of coffee.

Pure coffee is not well tolerated by everybody all the time because of its content of caffeine.

As a result there have been developed already, over a long period, processes for extracting caffeine almost completely from coffee. The caffeine must be extracted from the raw bean, since extraction of the roasted bean cannot be carried out without loss of aroma.

The most usual decaffeination process is effected in three phases.

1. Digestion:

The coffee beans are digested with superheated steam at an elevated temperature until their water content amounts to about 15 to 30% and as a result, the beans swell considerably.

2. Extraction:

The digested beans are treated with an organic solvent under constant mechanical agitation. As solvents, the following are, *inter alia*, recommended: benzene, ethyl acetate, isopropanol, chloroform, dichloroethylene and trichloroethylene.

3. Steaming:

After the caffeine has been largely extracted, the beans contain a considerable amount of the corresponding solvent, which must be completely removed. The procedure for solvent removal is tedious and comprises repeatedly steaming under pressure followed by releas-

ing the pressure until there are only traces of solvent left in the beans. Thereafter, the moist beans are then dried, either under vacuum or at elevated temperature with warm air.

It has now been found that the caffeine can be quantitatively removed from the raw coffee by treating the coffee with moist carbon dioxide in the super-critical state. The invention therefore provides a process for the decaffeination of coffee in which caffeine is removed from raw coffee by contacting said raw coffee with moist carbon dioxide in the supercritical state. It is to be understood by the expression "supercritical state" according to the invention that the carbon dioxide has a temperature above the critical temperature and simultaneously a pressure above the critical pressure of the carbon dioxide as described in the Austrian Patent 255,371. The observation that caffeine could be removed relatively easily from moist raw coffee by subjecting it to a supercritical gas phase was not expected, for the following reason.

The German Democratic Republic Patent No. 41,362 and also the corresponding British Patent No. 1,057,911 are concerned with processes for separating mixtures of substances by means of gases in the super-critical state. It is shown in Examples 61 and 62 thereof that substances which are dissolved in water or are present in an aqueous emulsion can only be taken up, with very great difficulty, in a gas in the super-critical state.

However, caffeine, dissolved in water, can be taken up relatively easily in gaseous carbon dioxide in the super-critical state, whereas dry caffeine is not.

The two afore-mentioned patents disclose that the supercritical gas used, is chemically inert towards the substances to be taken up or separated. Nonpolar gases in the super-critical state do not usually take up water. However, carbon dioxide is a nonpolar gas and yet it takes up water in its supercritical states. The probable reason for this

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unexpected behaviour is that carbon dioxide forms H_2CO_3 in the presence of water, which is taken up by excess supercritical carbon dioxide. Therefore, moist carbon dioxide in the supercritical state no longer has the properties of a nonpolar gas but rather those of a polar gas. In this form carbon dioxide is able to take up polar caffeine. Highly polar substances are not affected by nonpolar gases in their supercritical state, but only by polar gases in the same state, for example ammonia or dimethylether. Therefore, caffeine and its salts are not affected by pure carbon dioxide in supercritical status, but only by moist carbon dioxide.

The decaffeination process of the invention will be explained by reference to an example and by reference to the accompanying drawing.

Raw coffee B is disposed on a screening plate U in a pressurised vessel A containing water C in the bottom of said vessel. The pressurised vessel is heated by a water jacket to about 70°C . Carbon dioxide enters the pressurised vessel at D and is conducted through the vessel at a temperature of about 70°C and a pressure of about 160 atm. The carbon dioxide first of all bubbles through the water, whereby it is moistened with water and then flows through the coffee, where it gives off some of its water to the coffee beans and at the same time is charged with caffeine. The carbon dioxide, now charged both with water and caffeine, leaves the pressurised vessel A at E and is conveyed through heat exchanger F into pressurised vessel G, entering at H. The narrow upper portion of this pressurised vessel G is charged with an active carbon K and is heated by a water jacket to about 25°C . In the heat exchanger F, the charged super-critical carbon dioxide stream is cooled from about 70° to about 25°C , and as a result, liquification of the carbon dioxide occurs.

Carbon dioxide in the super-critical state takes up water at 70°C and in fact absorbs an amount several times greater than the amount expected when calculated on the basis of its vapour pressure at 70°C . When carbon dioxide is liquified in the heat exchanger by cooling, liquid water is simultaneously separated out, since water is only slightly soluble in liquid carbon dioxide at 25°C .

The stream containing a small amount of liquified water and a larger amount of liquified carbon dioxide and caffeine dissolved therein therefore enters the pressure separator G. Carbon dioxide and water pass through the active carbon, whereas the caffeine is quantitatively retained on the carbon. The liquid carbon dioxide and water leave the pressurised vessel G again at L and are returned by way of the valve M, the circulating pump N and the heat exchanger F into

the pressurised vessel A. The valve O is closed during the caffeine removal process.

After terminating the caffeine removal process, the valve M is closed while the valve O is opened. Then only liquid carbon dioxide discharges at P from the pressurised vessel G. At the same time, the water C which is still in the pressurised vessel A is drawn off through the valve R. Dry, super-critical carbon dioxide now enters the pressurised vessel A at D, and it becomes charged with the water which the raw coffee had taken up during the caffeine treatment. This water is collected at the bottom of the pressurised vessel G and can be drawn off through the valve S.

After completion of the drying operation, the carbon dioxide is drawn off through the valve T and the raw coffee, now free from caffeine and ready for roasting, is emptied pneumatically through the flange.

The process is preferably carried out at a temperature of 40 – 80°C and a pressure of 120 – 180 atm.

The decaffeination takes from 5 up to 30 hours and the subsequent drying from $1/2$ to 5 hours. The entire process takes more quickly at the higher temperature and the higher pressure.

It is not necessary to remove the caffeine by adsorption on active carbon from the circulating stream of carbon dioxide. It can also be separated out by expansion of the circulating carbon dioxide to a pressure below the critical pressure of the carbon dioxide, as is discussed in the aforementioned patents. In such a case, however, it is necessary for the carbon dioxide to be recompressed by a compressor. In the example as described above, however, it is only necessary to keep liquid carbon dioxide and some water in circulation by means of a piston pump or gearwheel pump.

Decaffeination of digested raw coffee by liquid carbon dioxide, at a temperature below the critical temperature of the carbon dioxide and below the corresponding pressure, is not suitable, since then not only caffeine, but considerable quantities of other substances which form the aroma when the coffee is roasted, are simultaneously extracted from the bean.

When the process of the invention, substantially only caffeine is removed from the bean. The residual content of caffeine in the raw coffee can in this way be reduced to below 0.01% .

The new process makes it possible for raw coffee to be converted in one step into caffeine-free coffee ready for roasting.

WHAT WE CLAIM IS:—

1. A process for the decaffeination of raw coffee which comprises contacting the raw coffee with moist carbon dioxide in the super-critical state to effect removal of



unexpected behaviour is that carbon dioxide forms H_2CO_3 in the presence of water, which is taken up by excess supercritical carbon dioxide. Therefore, moist carbon dioxide in the supercritical state no longer has the properties of a nonpolar gas but rather those of a polar gas. In this form carbon dioxide is able to take up polar caffeine. Highly polar substances are not affected by nonpolar gases in their supercritical state, but only by polar gases in the same state, for example ammonia or dimethylether. Therefore, caffeine and its salts are not affected by pure carbon dioxide in supercritical status, but only by moist carbon dioxide.

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The process is preferably carried out at a temperature of $40\text{--}80^\circ\text{C}$ and a pressure of $120\text{--}180$ atm.

The decaffeination takes from 5 up to 30 hours and the subsequent drying from $1/2$ to 5 hours. The entire process takes more quickly at the higher temperature and the higher pressure.

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2. A process as claimed in claim 1 in
which contact with the moist carbon dioxide
5 is effected at a temperature of from 40 to
80°C and under a pressure of 120 to 180
atmospheres.

3. A process as claimed in claim 1 in
which the contact with the moist carbon
10 dioxide is effected for a period of from 5 to
30 hours.

4. A process for the decaffeination of raw
coffee which comprises contacting the raw
coffee with moist carbon dioxide at a tem-
15 perature of 40 to 80°C and a pressure of
from 120 to 180 atmospheres for a period of

from 5 to 30 hours to effect removal of
caffeine therefrom and recovering a substan-
tially decaffeinated coffee.

5. A process as claimed in any of claims 20
1 to 4 substantially as herein described with
reference to the Example and the accompany-
ing drawing.

6. Decaffeinated coffee when produced by
a process as claimed in any of claims 1 to 5. 25

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