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<p>(21) International Application Number: PCT/US79/00854 (22) International Filing Date: 18 October 1979 (18.10.79) (71) Applicant: GENERAL FOODS CORPORATION [US/US]; 250 North Street, White Plains, NY 10625 (US). (72) Inventors: HUDAK, Stephen, Francis; 15 Hillside Avenue, Croton-on-Hudson, NY 10520 (US). SALEEB, Fouad, Zaki; 15 Gregory Place, Pleasantville, NY (US). (74) Agents: SULLIVAN, Thomas, V., et al.; General Foods Corporation, 250 North Street, White Plains, NY 10625 (US).</p>		<p>(81) Designated States: AT (European patent), BR, CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), JP, LU (European patent), MC, NL (European patent), SE (European patent), SU. Published <i>With international search report</i></p>
<p>(54) Title: AROMATIZED SOLUBLE COFFEE (57) Abstract Soluble coffee solids are processed to have a unique microporosity such that 3 to 30 microliters of the pore space per gram of solids are comprised of pores having a radius of 150 Å or less. The microporous soluble coffee solids act as an excellent sorbent for roasted and ground coffee aromas and, when admixed in small quantity with conventional soluble coffees, enhance the product with in-jar aroma.</p>		

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DescriptionAROMATIZED SOLUBLE COFFEETechnical Field

05 The present invention pertains to soluble
coffee and, more particularly, is directed to
freeze-dried soluble coffee solids. Specifically,
the invention is related to soluble coffee granules
having a unique porosity which provides these
10 granules with the capability of sorbing and retain-
ing roasted and ground coffee aromatics and control-
lably releasing these aromatic volatiles.

Background Art

15 Compared with roasted and ground coffee, the
source material, soluble coffee has very little
aroma.

Prior to the present invention, virtually all
commercial soluble coffee products have been en-
hanced with aromas by combining the soluble coffee
with pure coffee oil or aroma-enriched coffee oil in
20 an endeavor to provide the soluble coffee product
with an aromatic quality more akin to roasted and
ground coffee (cf. U.S.A. Patent No. 3,148,070).

Aromatizing soluble coffee solids with coffee
oil has several drawbacks. Many processing problems
25 are encountered in recovering the oil from the
roasted and ground coffee and, once obtained, the
glyceride has a tendency to become rancid. Also,



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coffee oil, even in small amounts, adversely affects the flowability of soluble coffee granules and undesirable droplets of the oil can, and do, appear on the surface of the liquid beverages prepared from the oil-containing soluble coffee solids.

Prior suggestions, trials and other efforts directed toward aromatizing soluble coffee solids without the use of coffee oil as the aroma carrier have not, within present knowledge, met with commercial success. These attempts have been less than successful, for the most part, because of the inherent lack of sufficient affinity of conventionally produced soluble coffee solids for sorbing and retaining volatile coffee aromatics.

15 Disclosure of the Invention

The thrust of the invention is the aromatization of soluble coffee products without the use of coffee oil. Surprisingly, it has been discovered that soluble coffee solids, produced under a condition which provides them with a unique porous structure, have an affinity of heretofore unrealized large magnitude for roasted and ground coffee aromas.

The porous soluble coffee particles of this invention not only have the capacity to sorb large quantities of volatile aromatics of roasted and ground coffee, but also have the capability to retain the aromatics for extended periods of time and subsequently, to release the aromatics under controlled conditions.

30 These highly aromatized soluble coffee particles, when added in small amounts, and uniformly admixed with typical unaromatized soluble coffee solids, provide the composite product with the desirable fragrant aroma of freshly roasted and ground coffee.



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The aromatized soluble coffee particles find their greatest utility as sorbent for roasted and ground coffee aromas which are to be released upon opening a jar of aroma-enhanced soluble coffee. When
05 the jar is recapped, the uniquely porous particles controllably release additional aromas which permeate the contained remaining bulk product and void spaces. On reopening the jar, the aromas are further released to the atmosphere foretelling the consumer
10 of an enjoyable beverage.

The essence of the invention resides in the discovery of a unique microporous structure which not only provides soluble coffee particles with available exposed internal surface areas for solid
15 surface to vapor molecular attraction (adsorption of the roasted and ground coffee aroma vapors) but also the structure manifests micropores within a range of sizes which extensively sorb and retain roasted and ground coffee aromatics via capillary condensation..
20 The molecular structures of the aromas "fit" and cooperate with the micropores to the extent the aromatics are releasably retained within the micropores substantially by capillary condensation forces and by some surface contact attracting
25 forces.

Condensation of the aromas affords the micropores the capability of sorbing significant quantities of aromatics which are, subsequently, controllably released as vapors.

30 For purposes of this invention, the term "micropore" is intended to mean a pore having a radius of 1000 Å or less.

In order to produce a satisfactory and successful result within the precepts of the invention, it
35 has been determined that the particles of soluble



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coffee to be initially aromatized with roasted and ground coffee aromas must have a porosity such that from 3 to 30 microliters per gram of the dry soluble coffee solids is comprised of micropores which have a radius of 150 Å or less. That is, the soluble coffee solids must have 0.3 to 3% (v/w) of useful pore space-pore space comprised of pores having a radius of 150 Å or less.

Inherently, when the soluble coffee solids are prepared so as to have from 0.3 to 3% (v/w) of the pore space comprised of pores having a radius of 150 Å or less (useful pore space for purposes of the invention), a gradation of pore sizes results with those pores having a radius of less than 30 Å most frequently occurring and contributing to the useful pore space.

The fact the useful pore space is comprised of pores of gradual sizes adds to the overall capability of the useful pore space to sorb and retain aromas associated with roasted and ground coffee. The aromas are a mixture of compounds of various molecular size and structure, each of which is preferentially sorbed and retained by capillary condensation in pores of a size most suitable for this purpose.

Those pores in the soluble coffee solids having a radius greater than 150 Å have been determined to be substantially incapable of sorbing any of the components of roasted and ground coffee aromas by capillary condensation and are, therefore, considered to be outside the useful range.

It has now been determined that from 0.05 to 20 milligrams of roasted and ground coffee aromas can be sorbed by capillary condensation per gram of dry coffee solids having a useful pore space of 0.3 to 3% (v/w).



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The specific amount of aromas sorbed is primarily a factor of the type aroma, the magnitude of the useful pore space, and the pore size distribution within the useful pore space.

05 Further, for those soluble coffee solids having a useful pore space of 30 microliters/gram of solids, when sorbing within each gram of soluble solids as much as 10 milligrams of dry aromas from roasted and
10 ground coffee via capillary condensation, it has been determined that only 30-35% of the useful pore space is filled with aroma components.

The capillary condensation forces which sorb and retain the aromas have been determined to be less than the aroma vapor pressure forces striving
15 to release the aroma from the useful pore space. Thus, upon confining a small quantity of the aromatized soluble coffee solids within a closed container, the aroma will be driven from the solids in vapor form until an equilibrium partial vapor
20 pressure is attained within the container. Upon opening the container the vaporized aroma is further released to the proximate atmosphere. Reclosing the container brings about a second equilibrium condition. Thus it can be appreciated that a readily calculated
25 small amount of aromatized microporous soluble coffee solids of the invention can be admixed and jarred with unaromatized conventional soluble coffee to provide sufficient roasted and ground aroma to pass from the aromatized solids into the headspace
30 of the jar and be released each time the jar is uncapped.

Measurement of Pore Size and Useful Pore Space

The porosity of a material is the ratio of the volume of the interstices of the material to the
35 volume of its mass. To extend this definition to include the number of interstices (pores), their



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shape and size (particularly micropores), requires sophisticated measurement and calculation techniques.

05 The characteristics of the porosity of the dry soluble coffee solids for the present invention have been calculated from responses from model systems employing CO₂ and N₂ gases according to the well recognized and authoritative methods of S. Brunauer, "The Adsorption of Gases and Vapors" Vol. 1
10 Princeton University Press, 1945 and Barrett, E.P., et al. Journal American Chemical Society 73 373 1951.

Best Mode for Carrying Out the Invention

15 The microporous particles of soluble coffee of the invention are prepared by shock freezing a concentrated coffee extract followed by freeze-drying the resultant frozen particles of extract.

20 Spraying an aqueous coffee extract, preferably, but not necessarily, having a soluble solids content less than 40% by weight, typically 25% to 35% by weight, into a cryogenic fluid having a temperature below -100°C, preferably liquid nitrogen, and subsequently freeze-drying the frozen particles of
25 solution produces dry microporous soluble coffee solids having the required useful pore space whereof from 3 to 30 microliters per gram of the solids is comprised of micropores which have a radius of 150 Å or less.

30 The spray should preferably produce particles having an average particle size of below about 200 microns diameter so that the entire particle will be instantaneously frozen on contact with the cryogenic fluid.



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It is not strictly essential the particle be formed from a spray or the particle size be below 200 μ --what is essential is the rapidity at which all of the moisture within the particle freezes.

05 It is believed that rapid freezing, approaching instantaneous, forms minute ice crystals exclusively throughout the particle. To assure this condition, the cryogenic fluid should have a temperature of -100°C or below.

10 The moisture content of the shock frozen particles of concentrated coffee extract which is in the form of minute ice crystals is sublimed from the particles to yield solid coffee granules with the microporous structure of the invention. It is essential that
15 moisture removal be accomplished substantially completely by sublimation (no liquid water present) to produce the desirable pore structure. Also, freeze-drying processing conditions must be carefully controlled to insure there is insignificantly little,
20 or no melting of the ice crystals during dehydration of the frozen coffee extract particles.

The aromas associated with roasted and ground coffee, whether natural or synthetic, may be derived from many sources well-known to those skilled in the
25 art. Depending on the method of contact to be employed, the aromas may be present as a component of a gas, a liquid condensate or a condensed frost.

The method of contacting the microporous particles with roasted ground coffee aromatics for
30 the purpose of sorbing aroma within the particles can also be many and varied. The use of high pressure and/or low particle temperatures may be employed in order to maximize the quantity of aroma sorbed or to



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shorten the period of time required to achieve a desired level of aromatization; however, such conditions are not usually required.

05 Among the techniques useful to date for the sorption of aromatics by the porous soluble coffee particles, the most preferable is to contact the microporous particles of soluble coffee with grinder gas frost (frozen roasted and ground aromatics plus frozen CO₂ obtained during the grinding of the
10 roasted coffee).

This is accomplished by placing both the porous particles and condensed CO₂ aroma frost well mixed in a vented vessel, preferably above -40°C, and permitting the CO₂ portion of the frost to sublime.

15 The microporous coffee granules of the invention have the capability of sorbing as much as 2% (w/w) of roasted and ground coffee aroma. This is, in general, in excess of that which is required and, depending on how the aromatized soluble coffee
20 solids are utilized, the aromatized particles will contain aromatics at a level of from 0.05 to 20 milligrams per gram of solids.

When the level of aromatics sorbed is 1 milligram/gram of aromatized solids, it requires about 5
25 grams of aromatized solids to be admixed with 95 grams of conventional soluble coffee to provide sufficient headspace aroma in the jar for release each time the jar is uncapped throughout the average periodic use of the beverage-making product.

30 Since it has been determined to be more preferable to admix 2% or less of aromatized microporous soluble coffee solids with the conventional soluble coffee, the aromatized mixture should preferably contain aromatics at a level of 0.2 to 0.5% (w/w).



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If the aromatized microporous soluble coffee granules are present in the product of the invention in excess quantity, they provide desirable flavor effects to the liquid beverage upon reconstitution of the granules with hot water.

As stated before, during storage of the aromatized soluble coffee granules admixed with the bulk unaromatized materials, the sorbed aromatics exert a vapor pressure which overcomes the porosity binding forces and a small quantity of aroma is released until a partial vapor pressure equilibrium condition exists within the jar. Upon opening the jar, the aroma is further released to the atmosphere foretelling the consumer of an enjoyable beverage.

Upon capping the jar, the aroma-retention and releasing processes are repeated. Thus, the inventive granules are capable of sorbing, retaining, and releasing roasted and ground coffee aromas to produce desirable soluble coffee jar package "head-space" aroma.

EXAMPLE

An aqueous coffee extract having a soluble solids content of 33% by weight was prepared by reconstituting spray dried coffee solids. This extract was sprayed into an open vessel containing liquid nitrogen whereupon the particles of extract immediately froze and were dispersed. The extract was sprayed by means of a two-fluid, glass atomizing nozzle (a chromatographic nozzle obtained from SGA Scientific, Inc., Fullerton, California) using air as the pressurizing fluid. The liquid nitrogen and particle mixture was poured into freeze drier trays, and the liquid nitrogen was allowed to boil off leaving behind a flat bed of frozen particles about



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1.16 to 3.2 mm. in thickness. The trays were placed in a freeze drier and subjected to a vacuum of 10 microns of Hg. and a plate temperature of 50°C for a period of 18 hours. The vacuum on the freeze drier was broken with dry CO₂ and the dry particles having a moisture content of below about 1.5% were removed from the freeze drier and kept out of contact of moisture. The dry particles were found to have a microporous structure such that 30 microliters per gram of coffee solids of the pore space were comprised of pores having a radius of 150 Å or less with the most frequently occurring pore size within the useable pore space being less than 30 Å.

The dry particles were subsequently chilled in dry ice under a dry atmosphere and mixed with coffee grinder gas frost, having a moisture content between 10 and 15% by weight, at a weight ratio of 0.2 parts frost per part particle. The mixture was transferred to a prechilled jar having a pinhole vent, and the jar was stored at 0°F overnight during which time CO₂ was evolved. The chilled particles, having a moisture content of below 6% by weight, were then packaged in glass jars with unplated, agglomerated spray-dried coffee solids at the level of 0.75% by weight of spray-dried solids. The resulting jars were then stored at 95°F. for periods of eight weeks. Upon initial opening and during a standard 7-day, in-use cycle, a pleasing headspace aroma was found which was rated as being at least as good as the headspace aroma possessed by jars of comparably stored, aromatized, agglomerated spray-dried coffee which coffee had been plated with grinder gas-enriched coffee oil. This oil-plated sample was prepared in accordance with U.S. Patent No.



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4,119,736 using an amount of grinder gas frost for each weight unit of soluble product comparable to that employed in the inventive sample.

As previously noted, jar aroma has been provided
05 to commercial soluble coffee products by means of oil plating an aroma-bearing glyceride (e.g. coffee oil onto soluble powder). It has also been contemplated to absorb coffee aromatics onto oil-plated soluble coffee, and this technique is expressly
10 disclosed in U.S. Patent No. 3,823,241 to Patel et al. It has, however, not previously been thought possible to sorb high levels of aromatics directly onto soluble coffee solids such that the aromatics would be retained. The Patel et al. patent notes
15 the criticality of the oil so that upon successive openings of the soluble coffee package (i.e., in-use cycle), the consumer will continue to perceive a jar aroma. This is in fact the situation for the conventional spray-dried, foam-dried and freeze-dried
20 products dealt with in the Patel et al. patent. However, the same deficiency does not exist with microporous soluble coffee particles having a useable pore space as described for this invention. As previously noted, conventional spray-dried coffee
25 does not possess a microporous structure; while in conventional freeze-dried coffee, most of the pore radii are on the order of 10,000 Å and the useable pore space (pores having a radius of 150 Å or less) is insignificantly small or entirely absent.

30 Industrial Applicability

The microporous soluble coffee granules of the invention find their greatest utility as sorbent for roasted and ground coffee aromas which are to be released upon opening a jar of soluble coffee. The
35 inventive product has no coffee oil as the aroma sorbent and thereby avoids the processing and physiological difficulties encountered with the



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glyceride. In this respect alone, the inventive soluble coffee product comprising packaged low or no aroma-containing soluble coffee admixed with a small amount of highly aroma-enhanced microporous soluble coffee granules represents a major technical advance in the art of soluble coffee manufacturing, particularly in view of the fact the aromas sorbed by the microporous granules have excellent stability during prolonged storage under inert conditions such as those which normally exist in packaged soluble coffee products.



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Claims

1. Freeze-dried microporous soluble coffee solids characterized by having from 3 to 30 microliters of pore space per gram of solids composed of pores having a radius of 150 Å or less.
2. The microporous soluble coffee solids of Claim 1 wherein the most frequently occurring pores composing the 3 to 30 microliters of pore space are pores having a radius of less than 30 Å.
3. A method for preparing freeze-dried microporous soluble coffee solids from a frozen spray of soluble coffee solids aqueous extract characterized by instantaneously freezing the spray droplets of 200 μ or less by contact with a cryogenic liquid maintained at a temperature of -100°C or below.
4. Microporous soluble coffee solids enhanced with added roasted and ground aromas characterized by having from 0.1 to 2% (w/w) of capillary condensed aromas releasably contained in those micropores having a radius of 150 Å or less and which constitute from 3 to 30 microliters of pore space per gram of solids.
5. A soluble coffee product, packaged within a reclosable container and enhanced with roasted and ground coffee aromas, characterized by having admixed therein from 0.1 to 5% by weight of the product, an aroma-enriched microporous soluble coffee sorbent, said sorbent having from 3 to 30 microliters of pore space per gram of sorbent consisting of pores having a radius of 150 Å or less.
6. The sorbent of Claim 5 wherein the most frequently occurring pores composing the 3 to 30 microliters of pore space are pores having a radius of less than 30 Å.



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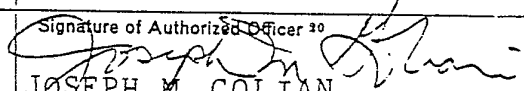
7. The sorbent of Claim 5 characterized by having from 0.2% to 1% by weight sorbed roasted and ground coffee aromas.

8. A method for enhancing soluble coffee with roasted and ground coffee aromas, characterized by enclosing said soluble coffee admixed with a volatile aroma-enriched microporous soluble coffee sorbent within a reclosable container, permitting said volatile aromas to gradually pass from said sorbent into the headspace of the container, whereby upon opening the container, the release of the coffee aroma volatiles from the headspace is detected.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US79/00854

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³				
According to International Patent Classification (IPC) or to both National Classification and IPC				
INT. CL A23F 5/32,5/46				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁴				
Classification System	Classification Symbols			
U.S.	426/594, 385, 386, 387, 388			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵				
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴				
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸		
X	US, A, 2,751,687, PUBLISHED 26 JUNE 1956, COLTON.	1-8		
X	US, A, 3,573,060, PUBLISHED 30 MARCH 1971, CASTEN ET AL.	1-8		
A	US, A, 3,660,115, PUBLISHED 02 MAY 1972, REVIE.	1-8		
A	US, A, 3,672,917, PUBLISHED 27 JUNE 1972, BUCHZIK.	1-8		
A	US, A, 3,765,904, PUBLISHED 16 OCTOBER 1973, DE ROISSART ET AL.	1-8		
A	N, SIVETZ ET AL, COFFEE PROCESSING TECHNOLOGY, 1963, THE AVI PUBLISHING COMPANY, INC.: WESTPORT, CONNECTICUT, U.S.A., VOLUME I-PAGES 240,241,244,245; VOLUME II-PAGES 138-141.	1-8		
A	N, SPICER, ADVANCES IN PRECONCENTRATION AND DEHYDRATION OF FOODS, 1974, JOHN WILEY AND SONS: NEW YORK, PAGE 415.	1-8		
<p>* Special categories of cited documents: ¹⁵</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </td> <td style="width: 50%; border: none;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </td> </tr> </table>			<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>
<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>			
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03 MAY 1980	12 MAY 1980			
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