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Legal Aspects

COFFEE

Volume 2: TECHNOLOGY

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The present volume, Volume 2 in
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of coffee, which described its nu
and various product forms.

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of green coffee and its subsequen
especially through extraction and
brewing of roasted and ground
possesses considerable mystique a
The choice of green coffees from
types available, through species/v
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understanding and guidance. Furth
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or instant coffee with little or
established. Finally, both the proc
leaving a range of different waste
etc.), and of roasted coffee after
spent coffee grounds, provide waste
commercial value in different ways

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Chapter 3

Decaffeination of Coffee

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Hoboken, New Jersey, USA

1. INTRODUCTION

Many of the physiological effects of coffee beverages are due to their caffeine content. The two major species of coffee, arabica and robusta, contain approximately 1 and 2% caffeine respectively. This corresponds to a cup of regular coffee containing on the average 85 mg of caffeine with a range of 50 to 150 mg based on preparation, blend and cup size.[1] A cup of instant coffee contains approximately half that of regular coffee with a reported range of 40 to 110 mg. To minimise the physiological effects and still obtain the desirable attributes of a coffee beverage, many procedures for caffeine removal have been proposed.

The process of removing caffeine from coffee was invented[2] by Dr Ludwig Roselius and Dr Karl Wimmer of the Kaffee-Handels-Aktien-Gesellschaft in Bremen, Germany. This invention is described in the German patent letter, DRP Deutsches Reich Patentschrift, dated from 1905. A commercial decaffeination process was implemented by the above company and they marketed a 'caffeine-free' coffee under the name of Kaffee Hag.

Around 1912, Roselius extended his business to the United States, and a coffee extraction plant was built at New Brunswick, New Jersey. During the First World War the American Kaffee Hag business was expropriated by the American government and the ownership of the company passed over to one Mr Gund, who moved the factory to Cleveland, Ohio. Mr Gund later sold his business to the Kellogg Company and the activities of the company were transferred to a 'million dollar plant' at Battle Creek, Michigan.

After the armistice, Roselius returned to the United States and started a new company, the Sanka Coffee Corporation. At first this company imported decaffeinated green coffee from Germany and roasted it in New York. Around 1927 Roselius made a deal with General Foods Corporation (The Postum Company) to conduct the Sanka business on a partnership basis. General Foods financed and equipped the Sanka factory in Brooklyn, New York. In 1932 Roselius sold his interest in the Sanka Coffee Corporation to General Foods Corporation, and General Foods became sole owner.

In December of 1937, General Foods Corporation purchased the American Kaffee Hag Company from the Kellogg Company, thereby gaining complete control of decaffeinated coffee in the United States and Canada at that time. About 1955 the Nestlé Corporation and others introduced decaffeinated coffee in the United States. In the 1970s General Foods Corporation bought the Kaffee Hag Company in Germany from the heirs of the aforementioned Dr Roselius.

Commercial decaffeination of coffee has mostly been performed on green coffee beans prior to roasting in order to minimise flavour and aroma problems. The desirable organoleptic properties of the beverage are developed after roasting. Allowing the decaffeination process to be performed on the green bean minimises aroma and flavour changes and losses. In addition, the two most common techniques are either based on solvent decaffeination or water decaffeination. Patent literature, however, also cites caffeine removal from roasted coffee extract.[3,4]

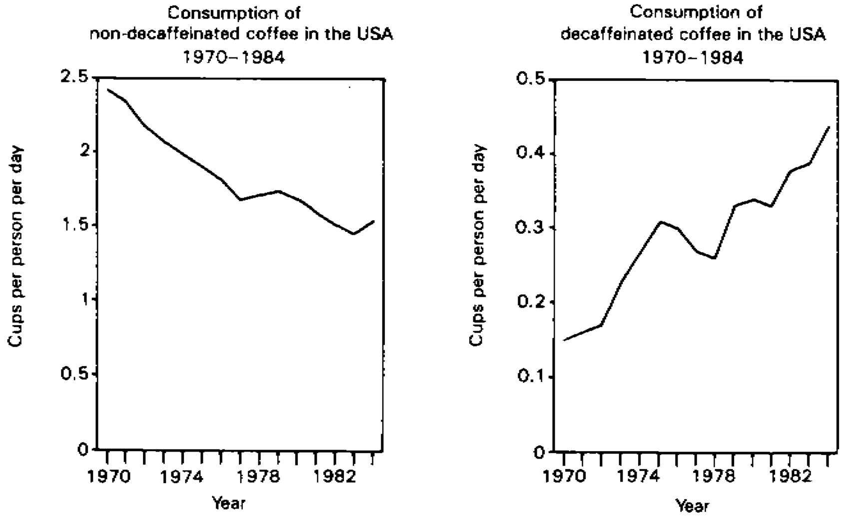

Fig. 1. Consumption of non-decaffeinated and decaffeinated coffee in the USA.

With the increased emphasis on health and health products and the known physiological effects of caffeine in coffee, more people are switching to beverages with less or no caffeine. As shown in Fig. 1 depicting the *per capita* consumption of coffee in the USA (approximately 50% of all coffee consumed), the number of cups of undecaffeinated coffee has been on a steady decline since 1970.[5] However, the *per capita* consumption of decaffeinated coffee has increased 153% in 12 years. The ratio of undecaffeinated to decaffeinated cups per person has dropped in this period from 16:1 to 4:1. With this continuous strong trend, the drive for the production of high-quality decaffeinated coffees produced in an economical and safe environment is stronger than ever.

2. SOLVENT DECAFFEINATION

Decaffeination of green coffee beans is still the preferred methodology used by most commercial coffee companies. The most direct approach to accomplish this is to contact pre-wetted green coffee with an appropriate solvent in conventional equipment in either a batch or continuous mode. Many solvents have been suggested for use in decaffeination of coffee beans or water extracts. Some of the criteria for the choice of solvent include the following:

(1) safety,
(2) cost of solvent,
(3) caffeine solubility,
(4) caffeine specificity,
(5) ease of solvent removal and recovery,
(6) toxicity and chemical reactivity,
(7) environmental effects.

Originally, benzene was used as the extraction solvent, but when trichloroethylene became available at reasonable prices, benzene was replaced by this non-flammable and less toxic solvent. As other chlorinated solvents were made available on a commercial basis, many coffee manufacturers switched to methylene chloride (dichloromethane), which has a higher caffeine solubility and a lower boiling point, allowing easier removal from the beans. Trichloroethylene has been under investigation by the US Food and Drugs Administration since 1976, and the only chlorinated solvent used either directly or indirectly is methylene chloride.

Table 1 lists most of the solvents that have been mentioned in US patents. Other than methylene chloride, the only known commercial solvents used are ethyl acetate,[6] coffee oil or other triglycerides,[7] and supercritical carbon dioxide.[8] The last of these will be discussed separately due to its unique processing requirements.

The basic principles of solvent removal of caffeine from green coffee are similar for any of the commercial solvents. The processes differ mainly in the methods of caffeine removal from the solvent and the methods of regenerating and recycling the solvent. If a volatile solvent is used, simple evaporation, usually in multi-effect or other low utility requirement evaporators, results in a clean solvent for recycling, leaving a caffeine-rich sludge to be refined. If a high-boiling solvent is used, either a water wash in a countercurrent liquid–liquid extractor or a high-vacuum sublimator is required, both to regenerate the relatively expensive solvent and to recover the valuable caffeine. Unlike most solvent extraction or degreasing operations the decaffeination of coffee beans requires the addition of significant quantities of water. A minimum water content of approximately 20% is required to be able to solvent-decaffeinate, and as much as 55% or saturation is used. Below 20% only limited decaffeination can occur no matter how much solvent is used.[9] Explanations for this phenomenon include softening and opening of the cellular structure to allow the caffeine to diffuse out of the bean. A more likely explanation involves the ability of caffeine to bond to the plentiful chlorogenic acid and its potassium salt, potassium chlorogenate, a complex ion-salt-like material that is essentially insoluble in the non-polar solvents commonly used.[10] Exceptions to this rule are aprotic solvents, but other problems preclude their use.[11]

Table 1
Selection of solvents mentioned in United States patents

Acetic ether
Alcohols
Aliphatic hydrocarbons
Benzene
Carbon dioxide
(liquid and supercritical)
Carbon tetrachloride
Chloroform
Coffee oil
Dichlorobenzene
Dichlorobenzol
Dichloroethylene
Dimethylsulphoxide
Esters (e.g. ethyl acetate)
Ethylene chloride
Fatty acids
Isopropylchloride
Ketones
Methylene chloride
Mineral acids
Mixed halogenated hydrocarbons
Paraffin oils
Sulphur hexafluoride
Tetrachloroethylene
Toluene
Trichloroethylene
Various fluorinated hydrocarbons
Vegetable oils

A typical solvent extraction process is shown in Fig. 2. In this semi-continuous process, fresh green coffee beans are steamed for half an hour, resulting in a moisture content of 16 to 18% w/w in the first column of a battery of columns. This is followed by a pre-wetting step to increase the coffee bean moisture to above 40% by weight. The wetted coffee beans are then countercurrently extracted by a solvent at temperatures between 50 and 120°C (120–250°F). The column from which most of the caffeine has been removed (95–98% decaffeinated) is isolated, solvent-drained and then steam-stripped to remove all residual solvent. Decaffeinated green beans are then discharged from the column and immediately dried before storage. Caffeine-rich solvent exiting from the fresh side of

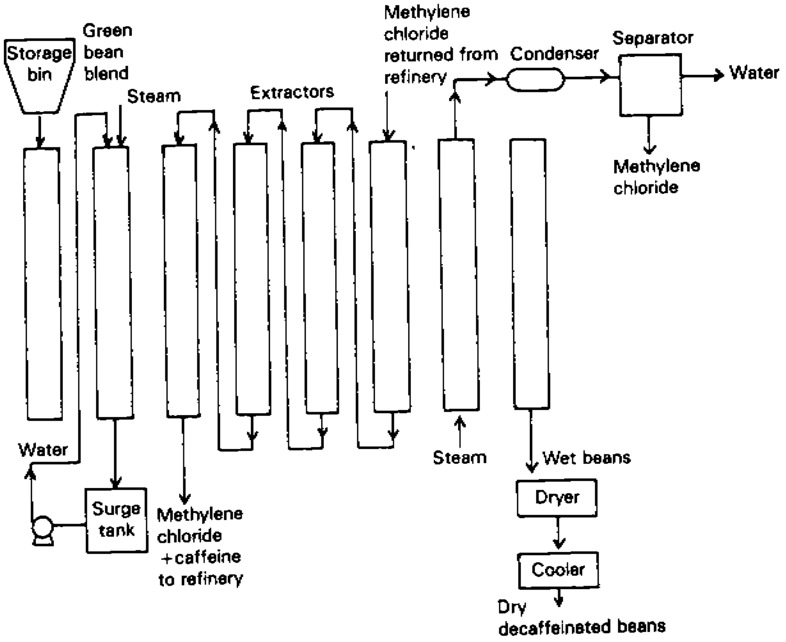

Fig. 2. Solvent decaffeination.

the column battery is then treated as discussed previously for caffeine recovery and solvent regeneration. Care must be taken to ensure that the solvent is saturated with water prior to recycling, in order not to dehydrate the pre-wetted coffee beans.

Typical operating conditions as stated in US Patent 3,671,263 are as follows:[12]

Steaming	30 min at 230°F
Pre-wetting	150°F to 42% water by weight
Caffeine extraction	Methylene chloride at 150°F for 10 h; 4 lb methylene chloride per pound of green coffee beans
Steam stripping	1·5 h

3. WATER DECAFFEINATION

A different approach to decaffeination of coffee beans was invented in 1941 by Berry and Walters of the General Foods Corporation.[13] This invention is based on using water to remove the caffeine from the bean. To prevent the extraction of all the water-soluble components of coffee beans, in excess of 20% by weight, the extraction water contains essentially equilibrium quantities of the non-caffeine soluble solids but no or very little caffeine. Claimed advantages include higher extraction rates, elimination of water-insoluble waxes extracted by the solvent, purer caffeine in a caffeine recovery system, and less heat treatment of coffee beans by the elimination of the solvent-stripping step since there is no contact between solvent and beans. An additional simplification in processing is the removal of the pre-steaming and pre-wetting steps, because all the water required to free the caffeine within the bean is supplied by the water extract. A flow sheet of the water decaffeination process is shown in Fig. 3. As in many coffee processing operations, use is made of a battery of columns in which green coffee beans are countercurrently extracted by a water extract containing about 15% solids other than caffeine. Water is absorbed preferentially by the dry beans during their residence in the extractors, and the solids concentration may increase to as high as 30%. Bean residence of approximately 8 h is required to remove about 98% of the original caffeine. Decaffeinated wet beans have about 53% by weight of moisture, and adhering solubles are washed with fresh water to minimise drying problems as well as to recover solids. This wash water is added to the caffeine-free water extract to bring the solids concentration back to the starting level of about 15%. Finally, the washed decaffeinated green beans are air-dried to be sold as a source of decaffeinated beans or processed in a conventional manner to produce decaffeinated regular roasted coffee or decaffeinated instant coffee.

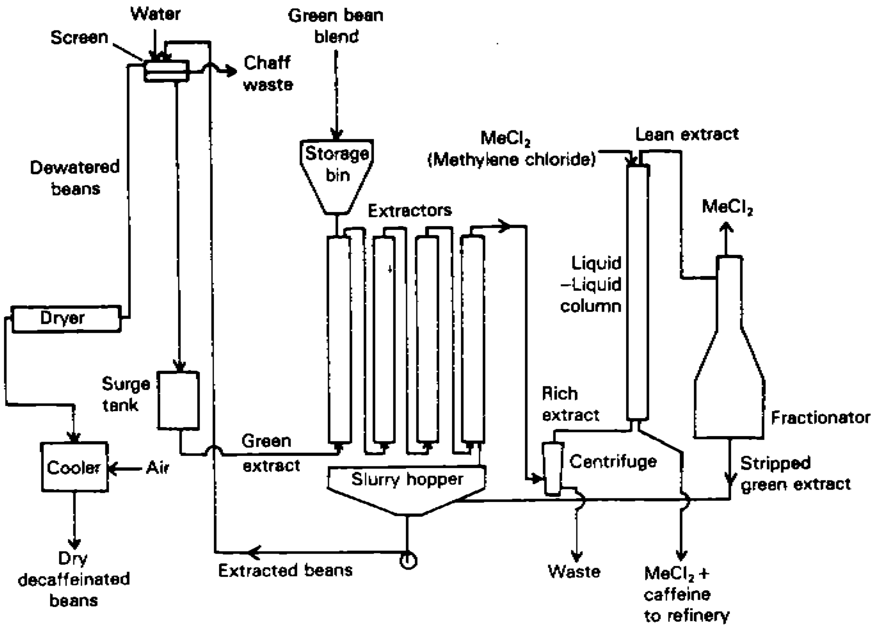

Fig. 3. Water decaffeination.

The extract, rich in caffeine (about 0·5% by weight), must be recycled after caffeine is removed in order to maintain the solids balance with other soluble solids contained in the green coffee beans. Caffeine is usually removed preferentially by contact with a specific solvent, but some newer patents have indicated improved developments in the use of solid adsorbents that have been suggested for at least 50 years. Caffeine-rich extract, after centrifuging to remove suspended solids such as coffee chaff, is contacted with an immiscible solvent such as methylene chloride to remove caffeine selectively. Any other solids extracted by the solvent are usually lost in the caffeine refining system. Various liquid–liquid contactors (extractors) have been tried, the most effective being a rotary disc contactor[14] to reduce the caffeine content of the green coffee extract to below 0·05% caffeine by weight. Countercurrent contact is performed by allowing the caffeine-rich extract to rise through the dense methylene chloride continuous phase at temperatures around 80°C (180°F) to take advantage of higher caffeine distribution coefficients and reduced emulsification problems at elevated temperatures. Extraction efficiency is controlled by the effect of the rotary disc speed on droplet size up to the point of column flooding. A solvent-to-extract ratio of about 4 to 8 is required to remove 99%+ of the caffeine from the extract. After solvent contact, the lean green coffee extract has dispersed and dissolved solvent in it that must be removed before it is allowed to contact coffee beans. Solvent removal is performed in a distillation column with feed to the top tray and reboiling and direct steam injection at the bottom to ensure complete solvent removal. Overs from the distillation column are at the azeotropic composition of the solvent, 98·5% by weight for methylene chloride, unless excess steam is used. Solvent, rich in caffeine exiting from the liquid–liquid column, is recovered by evaporation. Caffeine refining is discussed elsewhere. It is extremely important that all waste streams be very low in solvent content to meet environmental and legal requirements.

The use of adsorbent to remove caffeine in the past has not been economically useful as it has altered the quality of the final coffee detrimentally. A more recent claim overcoming these problems has been published in the European Patent Office by Coffex AG. This process utilises activated carbon that is preloaded with other coffee extract substances or with substitute substances of similar molecular structure or size, especially with carbohydrates, e.g. cane sugar, in order that the charcoal will take up as few extracted substances as possible. It is claimed for this procedure that, apart from caffeine, practically no other coffee components are removed from the green coffee. Decaffeination of the beans can be carried out either by total soluble solids extraction, decaffeination and reinfusion into the bean or by the use of the green extract procedure described above for a solvent system.

4. SUPERCRITICAL CARBON DIOXIDE DECAFFEINATION

The use of the solvent supercritical carbon dioxide for decaffeination of coffee, commercialised by HAG–GF in Germany, is based on the 1970 patent of Studiengesellschaft Kohle of Mulheim, Germany. Its use for decaffeination of green coffee beans is very similar to that of other solvents, with the major advantage of the use of an inert gas compressed to pressures high enough to increase caffeine solubility sufficiently for use in a closed cycle, as shown in Fig. 4. The major disadvantage is also due to the high pressures requiring costly equipment and batch processing. Bean preparation is basically the same as for other solvents, i.e. mechanical cleaning to remove dust and chaff followed by steaming and wetting to increase the moisture to a 30–50% range. The decaffeination process consists of loading the pre-moistened beans into the extractor vessel and at the same time solid adsorbent is loaded into the adsorption vessel. Sufficient carbon dioxide is loaded into the vessels and the circulation pump is started. The heat exchanger is used to increase temperature, thereby also increasing the pressure to the desired extraction level. As the carbon dioxide flows through the vessels, caffeine is extracted from the moist beans, and caffeine-rich carbon dioxide is recycled to the adsorber where caffeine is adsorbed on to the activated carbon. The caffeine-free carbon dioxide then starts a new cycle via the heat exchanger to the

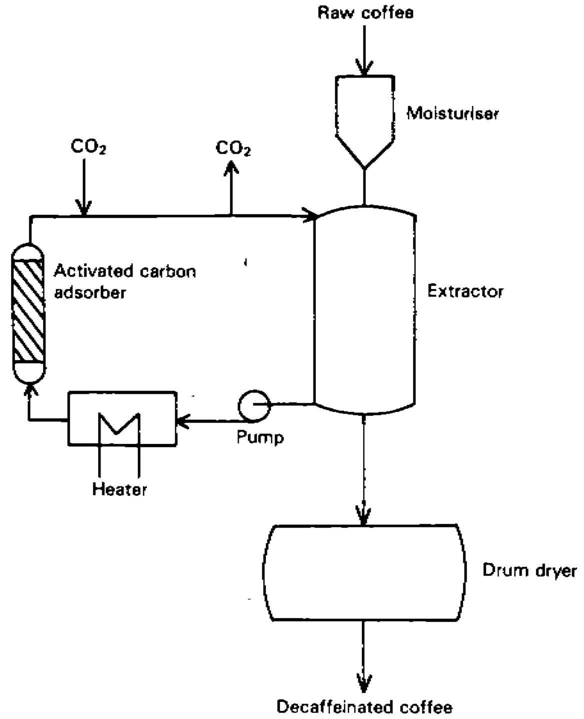

Fig. 4. Carbon dioxide decaffeination process, schematic.

extractor. Processing conditions are selected to minimise the extraction time to increase plant capacity and to improve process economics. The average concentration of caffeine in the carbon dioxide is low, requiring large quantities of carbon dioxide to be circulated. Therefore for energy conservation, equipment design is based on minimising pressure drop. At the conclusion of decaffeination the carbon dioxide is unloaded to a holding vessel and both the coffee beans and the adsorbent are unloaded from their respective vessels. The moist decaffeinated beans are then dried to approximately 10% water via a vacuum or hot-air drier. Further processing is the same as for any coffee bean. The supercritical carbon dioxide patent proposes use of moist carbon dioxide between 40°C and 80°C and pressures between 120 and 180 bars. It suggests caffeine removal from the carbon dioxide by lowering the temperature and or pressure to precipitate the caffeine due to lower solubility or to aid adsorption. Product quality is claimed to be improved because of the chemical stability and inertness of carbon dioxide preventing any reactions with the coffee constituents. In addition, supercritical carbon dioxide has a very high selectivity for caffeine, avoiding losses of non-caffeine solids. Product quality is claimed to be comparable to a regular undecaffeinated coffee due to the avoidance of any aroma/flavour precursor loss during the decaffeination process.

5. DECAFFEINATION OF ROASTED COFFEE AND EXTRACT

There are a number of advantages to the decaffeination of roasted coffee extracts.[15] These mainly deal with processing and equipment costs, especially with roasted extract used for the production of instant coffees. Since we are now dealing with the processing of essentially a finished product having good flavour and aroma qualities, most of the process efforts devoted to decaffeination must maintain and preserve these qualities. Usually the first steps include aroma stripping and collection via standard methods. These techniques are well documented in many patents[16] (see also Chapter 5, this volume). A major difficulty in the decaffeination of roasted extracts involves the loss of trace components to the contacting solvent necessary for flavour preservation. Two approaches to solve this problem in recent United States patents involve either the use of an inert, very specific solvent such as liquid or supercritical carbon dioxide for contacting the extract, or the use of a procedure of recovering these trace components by reflux and recycling back to the extract.[17] The latter procedure may also involve maintaining the level of these components in the solvent high enough to prevent extraction from the roasted extract. After decaffeination, processing is similar to the processing of undecaffeinated extract after adding back the stripped aromas.

6. CAFFEINE REFINING

The caffeine removed from coffee is a valuable commodity as a food or drug additive. At the present time the two main sources of caffeine are from coffee as a by-product of decaffeination and from a synthetic reaction between urea and chloroacetic acid. The price of caffeine is governed mainly by the cost of synthesis and demand. To refine coffee-sourced caffeine economically, the purity into a refining system must be in the order of 70% or better. Most of the procedures described above deliver a caffeine of 70 to 85% purity, and a refining system based on this purity was invented by Shuman in 1948. This process combines a number of purifying steps to eliminate various contaminants such as coffee waxes and oils, as well as caffeine-like water-soluble materials that impart a dark colour to a coarsely granular crystal instead of the desired white, needle-shaped crystals of pure caffeine.

The unrefined caffeine derived from the decaffeination process is usually obtained as a water solution or as dried cake. Any residual solvent is steam-distilled and the caffeine sludge that is formed is dissolved with recycled mother liquor from a centrifugation step in the refining process, as shown in Fig. 5. Activated carbon, recycled from a finishing step before final crystallisation, is added to remove most colour-contributing impurities. The slurry is filtered and the spent carbon is discarded or reactivated, or the caffeine may be recovered by use of acetic acid extraction.[18] At this stage the caffeine is 80 to 90% pure. A crystallisation step followed by centrifugation results in two streams. The crystals are redissolved for an additional purification step and the mother liquor is contacted with pure solvent to recover essentially all residual caffeine. Addition of aqueous alkaline solution can substantially aid this separation.[19] The decaffeinated mother liquor is discarded after the trace solvent is recovered. The solvent containing recovered caffeine is sent to an evaporator where it mixes with feed solvent used for decaffeination. Fresh activated carbon is added to the redissolved crystals. After filtration the

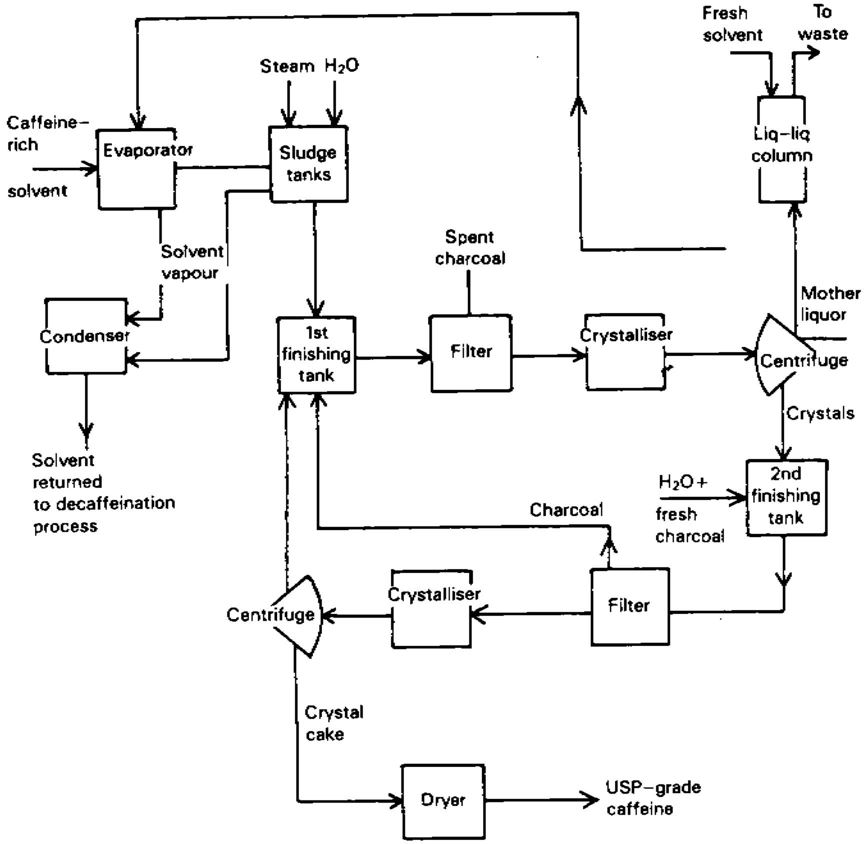

Fig. 5. Caffeine refining process.

carbon is recycled to the first finishing tank. A second crystallisation step followed by centrifugation yields a mother liquor that is recycled to the first finishing tank and a caffeine crystal cake. The cake is air-dried and broken to yield white USP-grade caffeine.

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COFFEE

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differential effects between them) while the extracts were in the slush-ice condition (i.e. extract temperature somewhat below 0°C). The foamed extract would only then be deep frozen, granulated and freeze-dried. The latter process became widely used in Europe and elsewhere, but General Foods in the USA continued to use a process for 'Maxim' giving granules of somewhat higher bulk density, packed in jars of significantly lesser volume for unit weight than other jars of instant coffee and described as 'concentrated'. By virtue of another General Foods patent claimed as prior art, General Foods challenged the validity of the Nestlé patent. Eventually, this matter was resolved out of court. From 1965 onwards, a large number of other patents were issued on freeze-drying and/or freeze-concentration from various companies (including Nestlé and General Foods). One such series was that of the Struthers International and Scientific Corporation (inventor N. Ganiaris), which was issued in the USA, the UK and elsewhere. Struthers were manufacturers of freeze-concentration equipment (ice crystallisation tube with internal scraper oscillator, and other designs). They worked initially as contractors for this purpose only for General Foods at their Hoboken, NJ, factory in 1964, but were replaced by another company in 1967. These patents covered the total freeze-drying process and individual aspects of it (e.g. freeze-concentrator design, handling of extracts, etc). Extensive litigation proceedings were initiated by General Foods in the UK and elsewhere in about 1971. An out-of-court settlement eventually proved necessary, largely on account of escalating costs. However, these particular patents are now only of historical interest.

7.4. Decaffeination Patents

Decaffeination, described in process detail in Volume 2, Chapter 3, has been a fruitful field for invention and therefore of coffee patents. This stems from the initial invention by Ludwig Roselius in Bremen, Germany, in 1905, who subsequently founded the company called Kaffee HAG by which name the product was also called. The original patent in 1905 described the preparation of decaffeinated roasted coffee by first pretreating the green coffee beans with steam, extracting the caffeine directly with an organic solvent such as benzene, steam distilling off the residual solvent and only then roasting. The patent was also filed in the USA, issuing in 1908 (USP 897 763 to Meyer, Roselius and Wimmer). Manufacture took place there, but was expropriated during the First World War and placed in US private hands, eventually passing to Kelloggs, and then to General Foods Corporation in 1937. However, Roselius returned to the USA shortly after that war to form the Sanka Coffee Corporation, which in turn was sold in 1932 to the Postum Company, eventually part of General Foods. Apart from Kaffee Hag in Germany, the Coffex company, based in Amsterdam and with many decaffeinating plants, dominated the decaffeination scene in Europe after the Second World War, essentially operating to supply decaffeinated coffee to other coffee roasters. The solvent in the original process changed to the use of substances such as ethyl acetate, and particularly the non-inflammable chlorinated hydrocarbons, of which only methylene dichloride is now used (1980s), and the only alternative process was so-called water decaffeination. In this latter process (General Foods, USP 2 309 092, 1943), recycled 'green' aqueous extract was used directly on the green beans. Caffeine was removed from the extract by the same kind of solvents as in the conventional process, which were therefore said to be used indirectly. It is important to note that in the direct process the green beans have to be impregnated with water first (30–35%), otherwise use of dry solvent will remove substantial amounts of the green coffee oil. Transfer of caffeine takes place mainly via dissolution into the aqueous phase and then into the organic solvent.

During the 1970s and onwards, a climate of opinion developed against the use of chlorinated hydrocarbons for decaffeination, whether used directly or indirectly, though the residual amounts of these solvents left in the green coffee (measured now by more sophisticated analytical methods such as GC and HPLC) have been found to be exceedingly small (i.e. < 1 ppm) and even less in derivative roasted products. Higher figures (i.e. up to 10 ppm) had previously been shown by cruder analytical techniques measuring total chlorine content. Numerous patents issued claiming use of a range of different organic solvents, though these were generally disadvantageous in one or more respects. However, patents also issued which were directed towards improving the conventional decaffeination process in respect of operating conditions to increase the rate of decaffeination (hitherto a rather time-consuming process), notably those of Procter & Gamble (USP 3 671 262–3 (1972), USP 3 700 464–5 (1973) and EP 0 114 426B (1987)), and of effective solvent removal (USP 4 530 900 (1985). Though methylene chloride has been declared safe for use,[15] there was an impetus towards processes not involving any chlorinated hydrocarbons. A further development of the original water process occurred, first by Coffex. In this the aqueous green coffee extract was denuded of its caffeine preferentially by use of activated carbon (neutral, acid or preloaded with other coffee extract substances or other carbohydrate substances) as described in EP 0 078 088A (Coffex, 1979); then Nestlé in EP 0 040 712A (1981, and B in 1985) with broad international coverage, e.g. USP 4 495 210A (1985), also USP 4 508 743A (1985); and General Foods Corporation, USP 4 298 736 (1981). An important aspect of these processes is the subsequent removal of the caffeine from the absorbent, and reactivation of the carbon if possible, e.g. USP 4 513 136 (General Foods, 1985). Adsorption by other materials has also been patented, e.g. Amberlite exchange resin, USP 4 031 251 (Nestlé, 1977) and Duolite, EP 0 078 088A (Douwe Egberts, 1982) also USP 4 113 887A (General Foods Corporation, 1979) and regenerating with carbon, EP 0 248 482A (Douwe Egberts, 1988).

There was a major technical departure in respect of the type of decaffeinating solvents used when Zosel at the Max Planck Institute of Coal Research in Mulheim, Germany filed a patent in 1970 (assigned to Studiengesellschaft Kohle GmbH, or SGK). This claimed a process of decaffeinating green beans by use of carbon dioxide made supercritical in the temperature range 40–80°C and pressure range 120–180 bar (1740–2610 psig). The supercritical point for carbon dioxide is 31·4°C and 75·2 bar. As with other organic solvents, it is necessary to have the green beans premoistened to about 30–35% w/w. The solubility of caffeine in the carbon dioxide is still low (about 1·5%) so that fairly large quantities of CO_2 have to be circulated, though it is assisted by the presence of moisture in the CO_2. Three means of caffeine release from the caffeine-loaded CO_2 were advocated, most preferably, for energy economics reasons, absorption on an activated carbon bed rather than temperature/pressure reduction and precipitation.

Supercritical CO_2 has been shown to have good selectivity for caffeine, leaving behind any water-soluble components of potential significance as aroma precursors on subsequent roasting of the decaffeinated green coffee. The process is unexceptionable in respect of solvent residues and has other advantages, but it is expensive in capital and sometimes running costs. This process, batchwise, was commercialised on a large scale by Kaffee HAG in the late 1970s in Bremen; the company was then bought by General Foods Corporation in 1980 and renamed HAG GF Aktiengesellschaft. In 1971 Zosel extended the range of his patent to include release of caffeine from the CO_2 by use of a system of repeated contact with water, which aqueous solution needed then to be evaporated for the recovery of the caffeine. In 1976 there was a third Zosel patent; in fact, the original 1970 patent has since spawned a large number of variants from other inventors in respect of other solvents in the supercritical condition but also of liquid CO_2 at high pressure; other substrates of coffee including roasted coffee and its extracts and green coffee aqueous extracts; and other operating conditions,

Table 7
Some patents for decaffeinating green coffee by use of supercritical/subcritical solvents

Country	*Patent or Application No.*	*Issue date*	*Applicant*	*Remarks*
West Germany	P 2 005 295	1973	SGK	Basic CO_2 supercritical patent
UK	1 290 117	1973		
USA				
Canada	926 693	1973		
Austria	40 033 171	1974	SGK	Absorption in water
USA	3 806 619	1974		
Austria	5 769	1976	SGK	Extraction/absorption (same vessel)
	7 806	1976		
	9 248	1976		
West Germany	P 2 212 281	1976	HAG	Liquid CO_2 at high pressure, but temperature <31·4°C
UK	1 372 667	1975		
USA	3 879 569	1975		
Canada	979 725	1976		
West Germany	P 2 634 525	1978	KVW	Use of N_2O plus water (ion exchange for release)
West Germany	P 2 637 197	1978	HAG	Ion exchange plus temperature change
West Germany	P 2 727 191	1979	HAG	Mixtures of solvents (e.g. 89 mol% CO_2 and 11 mol% acetone)
West Germany	P 2 737 793	1979	Peter (Erlangen)	Condensation of entrainer
West Germany	R 2 737 794 2 273 794C	1979 1986	Peter (Erlangen)	Very high pressure liquid
West Germany	P 2 846 976	1980	Krupps (Essen)	Use of supercritical propane
West Germany	P 2 848 582	1980	DEJ Int. (Utrecht)	Adsorption on synthetic polymer resins
USA	4 276 315	1979	General Foods	Liquid propane/butane
European	0 129 610A		HAG	Desorption of charcoal, (1) by hot water; (2) by formic acid
	0 129 609B	1986		
West Germany	3 213 636A	1986		

Table 8
Some patents for decaffeinating roast coffee and green and roasted coffee extracts under supercritical conditions

Country	*Patent or Application No.*	*Issue date*	*Applicant*	*Remarks*
West Germany	P 2119678[a]	1975	HAG	Roast ground coffee. Various solvents. Consecutive use of dry/wet
UK	1346134	1974		
USA	3843824	1975		
USA	877535[a]	1979	SGK	Thin film. Roast coffee extract
	906882[a]			
Japan	6058137B	1986		
USA	4246291	1979	General Foods	Various solvents. Desorption in water
European	0118019B	1986	HAG	Roast coffee. Subcritical temperature; ion exchange
European	0010637B	1982	Nestlé	Coffee extracts. Supercritical CO_2
USA	4251559A	1981		
West Germany	2953945B	1982		

[a] Application number.

especially those of the important aspect of means of release of the caffeine from the solvent. Tables 7 and 8 set out some of these patent issues in different countries. As explained in Volume 2, Chapter 3, decaffeination of roasted coffee and its extracts poses a number of extra problems to be solved in order for it to be satisfactory enough to be used commercially, so it is almost entirely green coffee that is decaffeinated and then roasted. An exception may be in the use of vegetable oils, particularly coffee oil, as a decaffeinating agent with some considerable advantages. Patents for this have issued, e.g. from Nestlé, West German Patent 2 651 128, with Patentschrift status in 1987, first published as Belgian Patent Application 848 635 with priority back in 1975 in the USA; see also Belgian Patent Application 835 556 in 1976.

7.5. Agglomeration Patents

Agglomeration of spray-dried particles (or during spray-drying) to give free-flowing granules was widely practised in the USA from about 1968 and in the UK from 1970, so that there is now a very high proportion of the instant coffee, whether freeze-dried or not, in the marketplace in this form. As might be expected, there has been considerable concurrent patenting activity, as indicated in Table 9 which has been updated from that in Volume 2 describing this process.

Table 9
Typical agglomeration patents for instant coffee

Patent No.	*Date*	*Assignee*
USP 2 977 203	1961	General Foods Corporation
3 554 760	1971	
3 615 670	1971	
3 695 165	1973	
USP 3 514 300	1970	Nestlé
BP 1 176 320	1967	
USP 3 679 416	1972	Chock Full o' Nuts Corporation
USP 3 966 975	1974	Niro Atomizer A/S
BP 1 385 192	1974	
USP 3 615 669	1971	Procter & Gamble
USP 4 594 256–8A	1986	General Foods Corporation
EP 0 207 384A	1987	Nestlé

7.6. Other Coffee Patents

In recent years there has been considerable activity in devising improved and also faster roasting methods; thus the fluidised bed for retail sales use, USP 4 489 506A (Wolverine Corporation, 1985), the 'bubbling bed' for controlled continuous roasting, USP 4 501 761A (General Foods Corporation, 1985), and an 'ultra-fast' method, EP 0 132 877A (Procter & Gamble, 1987).

Similarly in the packing of roast and ground coffee, where the twin problems of stability (due to the effect of oxygen in the headspace) and carbon dioxide release were fully discussed in Volume 2, Chapter 7, various in-pack absorbent materials have been proposed, e.g. EP 0036 575A (Mitsubishi, 1985), USP 4 552 767 (General Foods Corporation, 1985) and EP 0 192 364A (General Foods Corporation, 1987); all generally with wide other-country coverage. The conditioning of roasted coffee before grinding in an atmosphere of very low oxygen content, followed by equilibration in moist air, features in EP 0 092 803B (Illicaffe, 1986), and a follow-up of the original Kenco degassing patents appears in GB 2 128 068B (Kenco, 1986). Of interest is the soaking of raw coffee in fructose and/or sucrose solutions