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LITERATURE REVIEW

A review of anticaking agents in the realm of digital food printing

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Abstract

Background: Various food additives including anticaking agents have been in use since the second half of last century and digital printing of food is in practice. Concerns on food borne disease transmission following COVID-19 accelerated research in the direction of 3D printing. Objective: 3D printing of food depends on the rheological property of the dough. In addition to enhance the flow, anticaking agents which have other properties too can be exploited in 3D printing. Artificial intelligence (AI) assisted printing, targeting sustainability and customizability is in progress which needs data of food additives. The review has been done to consolidate data of the authorised anticaking agents used in food.

Methods: Using terms according to the criteria, a literature search was conducted with the data bases: Google Scholar, PubMed, ScienceDirect and Web of Science. Literature for full text analysis were selected from abstracts of 420 papers and books resulted on search, eliminating those prior to 2014, which were out of scope of the journal

Results: Consolidated literature about the anticaking agents authorised in Codex, is made discussing the deficiencies in the existing evaluation and highlighting the use of anticaking agents in 3D food printing. Promising application of the anticaking agents in AI assisted food printing has been observed.

Conclusion: This review being the first of its kind, consolidates the data of the anticaking agents including the current utility in 3D printing. It may instigate further research in this regard.

Keywords: Anticaking agents, 3D Food printing, Artificial intelligence, Ferrocyanides

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Introduction

Quality of food is not easily definable as it is based on its organoleptic characteristics and nutritional value. Food additives are substances that are added to food for particular purposes to increase the shelf life and to improve the customizability. Innovation in food technology has crossed nanoencapsulation, ultra processing and has reached up to a stage of AI assisted digital printing of food.

3D printing of food (additive manufacturing) involves computer controlled material deposition such that products with definite composition and microstructure are formed without much human intervention. It offers the users to fabricate more customized foods, which depends on the rheological properties of the food material, printing and post printing parameters.[1] The raw material for food printing need to be in a state that allows them to be easily printed, whether it is in liquid or powder form, but should possess flowing property.[2] 4D printing refers to the change of shape, physical or chemical properties and functionality of the printed material over time in an ingredient of the food product.[3] Anticaking agents enhance the flow of the host particles by reducing the tendency to adhere to one another and hence have definitely crucial role in the properties of the material to be printed. Thisbecomes all the more true in the sintering techniques which make use of the powder deposition.[4] Further, the anticaking agents have many other characteristic properties which may find printing applications. Most essential aspect of digital food printing lies in the selection and utilization of the ingredients and their compatibility with the printing process. Artificial intelligence, with the enriched data base manages the printing process ensuring high quality, safety and personalization of the food.[5] Substances that modify acidity, viscosity, flavour, texture, mouth feel or probiotics could be added to the basic ingredients namely; carbohydrates, proteins, fats to enhance their properties and nutritional value.[6] The scope of the review is to summarize the literature about the anticaking agents listed in Codex7 highlighting their applicability in 3D printing of food and to provide insights for researchers from both the fields of food additives and digital printing of food.

Methods

A systematic review of the anticaking agents used in food industry was conducted through the online databases (Google Scholar, PubMed, Science Direct, Web of Science). The key words used were 'Anticaking agent', 'Digital printing of food' 'AI and Food', in general and the name of the specific anticaking agent as listed in Codex. Searches were also done using the names with synonyms wherever necessary. Relevant data from 1940s were reviewed and those within the scope of the journal are incorporated. Appropriate data up to March 2024 are included after screening the literature by title and abstract followed by full text review.

Anticaking Agents

The use of substances to prevent clumping predates written records and probably natural substances like flour might be used to prevent caking. Beyond preventing caking, the interest was to develop anticaking agents that offer additional benefits. There are 34 substances listed in the functional category of 'anticaking agents' in Codex including 7 exclusive anticaking agents. The rest of the compounds have more functions which consist of 16 emulsifying agents, 15 each of stabilizers and thickeners, 14 acidity regulators, 7 raising agents, 6 each of glazing agents and humectants, 5 flour treatment agents, 4 each of bulking agents and carriers, 3 each of firming agents, and colouring agents, 2 each of sweetening agents and antifoaming agents, 1 each of flavour enhancer, foaming agent and sequestrant7. An anticaking agent by technological perspective may be an anti-stick agent, drying agent or a dusting agent. Though advancement has reached up to microencapsulation for many of them, no data was available on some and hence are excluded in the review. We have discussed the anticaking agents under different groups, though not done so in Codex. All the additives are discussed with International Numbering System (INS) numbers along with Chemical Abstract Numbers (CAS). Table 1 summarises the important anticaking agents discussed in the review.

Carbonates, bicarbonate and sesquicarbona

Calcium carbonate [170(i): (CAS: 471-34-1)], sodium carbonate [500(i): (CAS: 497-18-8)] and magnesium carbonate [504(i): (CAS: 546-93-0)] are natural, hygroscopic substances with established safety profiles. Carbonates of calcium and magnesium are authorised flour treatment agents. Hickman et al[9], reported that biogenic

Table 1. Summary of the major anticaking agents discussed in the review

Anticaking agent	INS number	CAS number	Other functions*	Status in digital printing of food
Calcium carbonate	170(i)	471-34-1	Ar, C, Fa, Ft, S	White pigment in food printing ink
Sodium carbonate	500(i)	497-18-8	Ar, Ea, Ra, S,T	Altering gelation rheology and texture
Magnesium carbonate		546-93-0	Ar,C,Ft	Not used
Sodium bicarbonate	500(ii)	144-55-8	Ar,Ra,S,T	Used as smart ingredient for 4D printing
Monocalcium phosphate	341(i)	7758-23-8	Ar, Ea, Fa, Ft, H, Ra, S, Sa,T	High prospects in 3D printing
Dicalcium phosphate	341(ii)	7757-93-9	Ar, Ea, Fa, Ft, H, Ra, S,T	High prospects in 3D printing
Tricalcium phosphate	341(iii)	7758-87-4	Ar, Ea, Fa, Ft, H, Ra, S,T	High prospects in 3D printing
Hydroxypropyl distarch phosphate	1442	53124-00-8	Ea, S,T	Under research for flow property modification
Synthetic amorphous silica	551	7631-86-9	Af, Ca	Under research for preventing solidification
Calcium silicate	552	1344-95-2	Nil	Used in 3D printing as part of baking powder
Polydimethyl siloxane	900	9006-65-9	Af, Ea	No use
Cellulose	460(ii)	9004-34-6	Ba, Ca, Ea, Fa, Ga, S, T	Used as rheological modifier
Mannitol	421	69-65-8	Ba, H, St, Sw, T	Used as rheological modifier
Isomalt	953	64519-82-0	Ba, Fa, Ga, Sw, T	Used as sweetening agent
Magnesium stearate	470(iii)	557-04-0	Ea,T	Used for chocolate printing
Carnauba wax	903	8015-86-9	Ar, Ba, Ca, Ga	Used for enhancement of appearance and texture
Ferric ammonium citrate	381	1185-57-5	Nil	Used as anticaking agent for common salt which modify the viscoelastic properties of gels
Cyanides of sodium, potassium and calcium	535,536,538	14434-22-1 14459-95-1 1327-39-5	Nil	Used as anticaking agent for common salt which modify the viscoelastic properties of gels

*Af-antifoamimg agent; Ar-acidity regulator; Ba-bulking agent; Co-Colouring agent; Ca-carrier; Ea –emulsifying agent; Fa-firming agent; :Ft-flour treatment; Ga-glazing agent; H-humectants; Ra-raising agent; S-stabilizer; Sq- sequestrating agent; Sw –sweetener; T- thickener

carbonates are reported to have, sustainability and green credentials making them very prospective agents in the 3D printing of foods. Non edible food wastes containing calcium carbonate are reported as suitable ink for extrusion 3D printing. Calcium carbonate is used in the edible ink formulations as a white pigment and is also reported to reduce caking to improve the fluidity of tamarind paste at various concentrations.

Sodium carbonate, bicarbonate and the sesquicarbonate have been used as raising agents.[7-12]

The interaction between starch and gluten is affected by sodium carbonate and sodium bicarbonate with the increase of the swelling power and dough development time. The alkaline solution containing sodium carbonate and potassium carbonate named 'kansui' have been traditionally used to regulate the acidity and rheology of dough.[13-15]

In an investigation of the effect of sodium bicarbonate (baking soda) [500(ii) (CAS: 144-55-8)] on meat protein, Lizou et al.,[16] reported that it overall enhanced the processing performance of the meat. The leavening effect of it finds use in 4D printing.[17] The pH change time during mixing and bench time may be exploited in 4D printing especially for instant preparations.[3,18] 4D printed food need a smart ingredient and a stimulus ingredient which reacts to environmental stimuli, human intervention or internal stimuli. Sodium bicarbonate is a smart ingredient and is reportedto cause spontaneous change of the colour of natural powders exemplifying 4D printing.[3, 19] Carbonate and bicarbonate additives as such can be used in food only when they have low moisture content

and encapsulated carbonate based materials with a coating of lecithin, mineral or vegetable oil when the moisture is high as in cheese.[20]

Since digital printing of starchy foods is common, care is to be taken on the release of toxic acrylamide, an invariable product formed during frying and baking of starch in presence of sodium bicarbonate.[21] While using magnesium hydroxide carbonate, it is to be noted that it inactivate yeast, impart bitter taste and change the rheology of the dough badly.

The natural non marine evaporate mineral, sodium sesquicarbonate[500(iii)(CAS:533-96-0)] containing 90-95% of sodium bicarbonate, named 'trona' has been used as food tenderizer.[22]

Phosphates

Technological details of baking are out of scope of the review but involve lot of chemistry of phosphates. Phosphates have a series of excellent physicochemical properties. Phosphate additives are good acidity regulators that match pH 4-12. Further, the excellent water holding capacity, increased emulsification power, strengthening effect on protein, chelating effect on ions of copper and iron, leavening effect of the acidic phosphates, the cryoprotective power, texture development capacity, the foam stability and mineral nutritional enhancement make them versatile food additives which may find use in 3D printing.[6,18,23] Majority of packed food stuffs including baby formulae contain added phosphate.[24-25] Monocalcium monophosphate (MCP) [341(i) (CAS: 7758-23-8)] and dicalcium phosphates (DCP) [341(ii CAS: 7757-93-9] are hygroscopic white crystalline or granular powders. The hydrated form of MCP is fast acting and is used in combination with slower acting leavening agents. MCP is cited in more than hundred patented inventions disclosed on leavening agents.[26] DCP is used in combination with other phosphates and sodium bicarbonate, which require a baking time in excess of 30 min. It is used along with a faster acting raising agent where it provides last minute expansion of the cake batter. Microcrystalline form of tricalcium phosphate (TCP) [341(iii) (CAS 7758-87-4)] is thermally more stable and reacts only very slowly with water vapour or moisture during storage and hence used as an anticaking agent in dry beverage mixes. AI has been in use for whisky productionand one can expect developments towards 3D printing also in near future.[27] Food grade phosphates have been reviewed on their properties and uses.[28]

TCP has larger specific surface area and hence commonly used to bind water. Since moisture content of printing inks significantly affects the physical properties of food materials, TCP may find use in 3D printing.[29] The moisture absorption capacity of TCP is utilised in extending the shelf life of many fruit products.[30] The physical characteristics of amorphous and crystalline coconut sugar powder after the addition of TCP were studied by Nurhadi et al. TCP was found significantly to reduce water sorption of the coconut sugar powder.[31]

Starchy materials are often employed as printing inks and hydroxypropyl distarch phosphate (HDSP)[1442 (CAS: 53124-00-8)] is a prospective ingredient in digital printing. It is insoluble in cold water and has the properties of both cross linked starch and hydroxypropyl starch with excellent shear and acid resistance and stability to heat.[32] HDSP exists in various forms and is mainly used to prevent water leakage from frozen foods and to improve stability of sauces, processed meat and dairy products. Diet rich in it is dysphagia friendly and hence satisfies the requirements for personalized food.[33] It is suggested to have beneficial implications in the treatment of obesity. Zhang et al.,[34] reported inhibitory effect of HDSP on the retrogradation properties of sterilized pea starch jelly. Very recently Xu et al.[35] reported the use of HDSP in 3D printing of ice cream inks. Phosphates in ultra processed food is suspected to cause many diseases like type 2 diabetes and chronic kidney disease.[36-37] Nutritional requirements of astronauts during long-term stay utilize fruits, vegetables, meat products and nutrients as printing ingredients but the 3D printing is still limited due to technological limitations38. The outstanding properties of phosphate may be technologically explored with due consideration to the adverse effects too.[39]

Silicon derivatives

Silica, silicates and polydimethyl siloxane(PDMS) fit in this category of anticaking agents. Synthetic amorphous silica (SAS)[551 (CAS: 7631-86-9)] is a white fluffy amorphous powder or granules consisting of agglomerated aggregates greater than 100nm. Among various forms of silica, only SAS is authorised as a food additive. It can be used according to good manufacturing practice, in large categories of foods.[40-41] Calcium silicate[552 (CAS 1344-95-2)] is a water insoluble white fine powder capable of high water and oil absorption capacity due to the porous structure and hence can compete with the host powder for existing moisture in the environment.[42] In a study on the effect of anticaking agents and relative humidity on the physical and chemical stability of powdered vitamin C using different anticaking agents in various ratios Lipasek et al.,[43] observed that calcium silicate and silicon dioxide, 50% by weight, improved the physical stability of sodium ascorbate. Calcium silicate and magnesium silicate are reported to lower free fatty acids from cooking oils.[44] Calcium silicate being a part of baking powder is being used in 3D printing of food.[8]

Polydimethylsiloxane (PDMS) [900 (CAS: 9006-65-9)] is a non nutritional, processing aid, added to oils as an antifoaming agent. The capacity of PDMS to protect oils from oxidation during deep frying operations has been studied extensively.[45] The Acceptable Daily Intake (ADI) for PDMS is not fixed even after half a century of evaluations.[46]

Carbohydrate compounds

Microcrystalline cellulose (MCC)[460 (ii) (CAS: 9004-34-6)][, powdered cellulose [460 (ii) (CAS: 9004-34-6)], mannitol[421 (CAS: 69-65-8)] and isomalt [953 (CAS: 64519-82-0)] are carbohydrate anticaking agents specified.[7] Microcrystalline cellulose and powdered cellulose are essentially the same, only slightly differing in the specifications. Cellulose without chemical modification are practically useless in 3D printing as they thermally decompose before getting melted and become flowable but surface modified MCC finds applications in 3D printing.[47-48] Various carbohydrates such as gelatine, wheat flour and starch serve as printing materials in 3D food printing.[6] MCC dietary fibres have similarity in texture to fat and have been used to prepare low fat mayonnaise emulsion with required consistency, thermal stability and improved antioxidant and flow characteristics.[49]

The carbohydrate alcohols mannitol and isomalt are ‘bulk sweeteners’ which can provide volume and mouth feel.[7] They are orally non fermentable and hence noncariogenic carbohydrate sweeteners due to the low calories.[50] Kou et al.,[51] reportedexcellent anticaking effect of mannitol compared to stearates of calcium and magnesium. Ruiz-Ojeda et al.,[52] reported that isomalt could increase the number of bifida bacteria in human gut. Isomalt absorbs very little water during storage and well suited for wafers and has stability in baking with no browning. It helps to maintain the shape and structure of the

3D printed food.[53] It is very suitable for people who are willing to make moderate life-style change in the diet and can be blend with other sweeteners to adjust the intensity of sweetness.[50,54] Isomalt is expected to be explored in research for the production of personalized food. The cooling effect in mouth and sweetness of mannitol and isomalt make them important constituents of health mints and cough drops.[6,55] While considering isomalt and mannitol for digital printing, the side effects of the sugar alcohols namely osmotic diarrhoea and bloating effect are to be considered.[56]

Salts of fatty acids and Carnauba Wax

Salts of myristic, palmitic and stearic acids with ammonia, calcium, potassium and sodium (470(i)); salts of oleic acid with calcium, potassium and sodium (470(ii)) and magnesium stearate [(470(iii) CAS:557-04-0, 91031-63-9)] are the authorised anticaking agents with other suitable printing functions, especially chocolates, which is a food material used with a certain degree of success in 3D printing.[57] Among the salts of fatty acids, magnesium stearate is in fact a mixture with magnesium palmitate has been incorporated into chocolate inks and chewing gum formulations for 3D printing.[58,59]

Carnauba wax [903 (CAS: 8015-86-9)] with an ADI 7mg/kg bw/day is used in digital printing as a coating agent and to provide glossy finish to enhance stability and viscosity.[6,60] When used in food, it is not significantly absorbed from diet and even if absorbed, would be hydrolysed and the products are incorporated in to metabolic pathways.[61] Many reports are seen about the use of carnauba wax in enhancing the shelf life of fruits.[59,62] Carnauba wax was tested for encapsulation of water-soluble compounds and as a matrix in microencapsulation of flavours.[63]

Other Anticaking agents

Out of the anticaking agents authorised in Codex, ferric ammonium citrate [381); (CAS :1185-57-5)] and ferrocyanides of sodium, potassium and calcium [535, 536 and 538)(CAS 14434-22-1, 14459-95-1,and 1327-39-5)] are not directly used in 3D printing, but used in sodium chloride which modify the viscoelastic properties of the gel.[6,2] Ferric ammonium citrate is a green powder with a faint odour of ammonia and saline ferruginous taste is authorised as an anticaking agent, nutrient, dietary supplement and acidity regulator.[7] The specifications for sodium ferrocyanide, potassium ferrocyanide, and calcium ferrocyanide have been established.[64] In the presence of ferrocyanides, sodium chloride crystals grow dendritically instead of its native cubic form and when a salt contains one or more ferrocyanide salts as anticaking agents, the term ‘ dendritic’ should be included.[7] The mechanisms of the anticaking effect of the ferrocyanide on sodium chloride were studied in details.[65] The group ADI is fixed for sodium, potassium and calcium ferrocyanide as 0.03 mg/kg/ day expressed as ferrocyanide ion on the assumption that the absorption of ferrocyanides from the gastrointestinal(GI) tract is low.[64] The use of ferrocyanides in salt is much debated.[66-67] Based on the toxicity studies done in a span of 8 decades, using bacteria, animals and humans; Joint FAO/WHO Expert Committee on Food Additives (JECFA) arrived at a conclusion that ferrocyanides are safe at the present use level.

Discussion

Changing food habits with advancing technology has brought with it thousands of approved food additives though with controversy on the use and use levels of some of them.[8] Out of different categories of additives authorised, only substances under the functional category of anticaking agents have been reviewed here focussing on the properties of them and their use in digital printing of food. Evaluation of an additive is a long procedure some of which needed decades and still resulted in confusions and difference in specifications by various regulating bodies exist.[46,64,68] A group ADI for sodium, potassium and calcium ferrocyanides is fixed, but calcium ferrocyanide was used in none of the toxicological studies though they vary widely in their action towards heat.[64] Ferrocyanides are not involved in the normal biological processes. Further, infrared lasers employed in the sintering process in 3D printing may decompose the ferrocyanide ion and release cyanide, if not precisely controlled.

Artificially sweetened beverages, ice creams, industrial sandwiches, biscuits and cakes are the most frequently used categories of food and these contain some clusters of additives but no detailed studies are seen on the interaction between them.[69]

3D printing of food aiming at automation, customizability and sustainability in the food sector has a history of only few years thrust mainly on the most frequently used categories of food. The most important parameter in the success of 3D printing is the ingredient selection for which the physico-chemical properties of substances are to be well understood.[2] Currently carbonates, bicarbonates, stearates, carbohydrates, calcium silicate as part of baking powder, HDSP and carnauba wax are found used in 3D printing of food but only limited research literature is available on the uses of anticaking agents. Due to the multifaceted properties, phosphates seem to have of immense potential in 3D and 4D printing of food. AI has prospects in design, production, quality control and sustainability in digital printing leading to personalized foods.[27] To achieve the goal, many limitations are to be attended.

Food safety discussions on 3D printed foods are in the early stages. Rigorous safety standards are to be accepted in the printing components and printers in order to avoid contamination with bacteria that may lead to food borne diseases. Further, nutritional value of the food and the micro biome may also be affected. Intestinal micro biome plays a very important role in modulating risk of many diseases.[70, 71] The texture of printed food differs from the conventional food, indigestion, osmotic diarrhoea and blotting may result. Short term consumption can cause food poisoning, whereas use of it for long term can result in permanent changes within the body.[72] Selection and utilization of the printing materials and their compatibility with the printing process is to be thoroughly monitored.[6,21]

More data on; environmentally sustainable sourcing materials, particle size of additives, health effects due to the printed food, the effect of inorganic salts in dough properties, cause and effect relationship between consumption and effect of substances, effect of dietary components on gut microbiota and microencapsulation of additives are the bare minimum requirement of AI in 4D printing of food.[2,22,28] This together with the incorporation of bio medical data of diseases like coronary artery disease, chronic kidney disease, cancer and metabolic disorders which are common due to food additives are inevitable for successful AI assisted food printing in future.

Conclusion

Food habits often change with changes in technology. Processed food manufacture was triggered by the discovery of making bread. Later ultra processed foods entered the market on the shoulders of thousands of food additives of various categories which are merely used to improve the shelf life and palatability of food without proper health risk assessments. Anticaking agents were incorporated in to food to enhance the flow many of which have other desirable properties. A systematic review of literature about the anticaking agents authorised in Codex, is made discussing the limitations in the existing specification and highlighting the scope of them in digital printing of food.

3D printing of food which presently depends on the rheological properties has a history of only less than two decades and the food manufacture is on the way to 4D and 5D printing incorporating AI which aims at automation, sustainability, customizability and precise ingredient control. Ingredient control and automation can only be attained by feeding maximum relevant data of all categories of food additives and other desirable dietary materials. It is the first exhaustive review in this regard and may instigate further research to yield much more appreciable output. Though, no time frame can be set, AI assisted food printing can increase customizability and sustainability reducing health risks.

Conflict of interest

The authors declare that there is no conflict of interest.

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