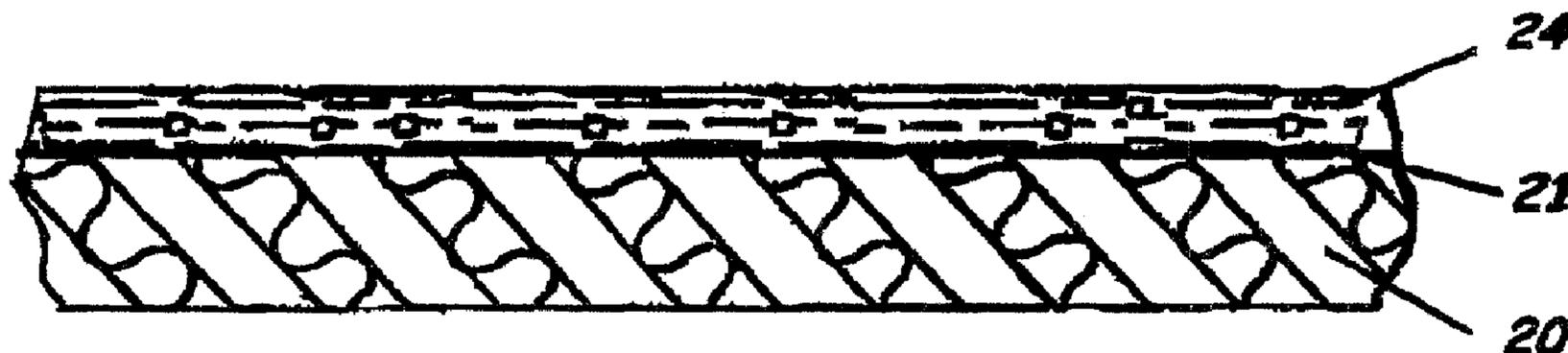




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(54) Titre : PAPIER DE PROTECTION CONTRE DES CORPS GRAS EXEMPTS DE FLUOROCARBURES  
 COMPORTANT UNE PELLICULE SOUPLE A BASE D'AMIDON ET METHODES POUR LE PRODUIRE  
 (54) Title: NON-FLUOROCARBON PAPER HAVING FLEXIBLE STARCH-BASED FILM AND METHODS OF  
 PRODUCING SAME



(57) **Abrégé/Abstract:**

A non-fluorocarbon oil and grease barrier paper for use particularly with products that need oil and grease resistant characteristics and are used in high or low temperature applications. The barrier paper does not contain fluorocarbons, which improves the environmental rating of the oil and grease barrier paper. The paper is made by applying a starch based coating having a solids content in a range about 10% to about 35% to a substrate. The starch based coating preferably contains a starch derivative, a flexibility enhancing agent, a rheological agent, and a scorch resistant agent. When the paper is heated, no fluorocarbons are emitted as result of heating the paper.

**NON-FLUOROCARBON PAPER  
HAVING FLEXIBLE STARCH-BASED FILM  
AND METHODS OF PRODUCING SAME**

**ABSTRACT OF THE DISCLOSURE**

5           A non-fluorocarbon oil and grease barrier paper for use particularly with  
products that need oil and grease resistant characteristics and are used in high or low  
temperature applications. The barrier paper does not contain fluorocarbons, which  
improves the environmental rating of the oil and grease barrier paper. The paper is  
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paper.

**NON-FLUOROCARBON PAPER  
HAVING FLEXIBLE STARCH-BASED FILM  
AND METHODS OF PRODUCING SAME**

5

**BACKGROUND OF THE INVENTION**

10    **1.       Field of the Invention**

[0001] The invention relates to methods for forming a non-fluorocarbon treated substrate having oil and grease resistant properties and to the resulting substrate end product.

**2.       Description of Related Art**

15    [0002] Paper products can be coated with various materials to increase certain properties of the paper. This is particularly true, for example, if the paper product is utilized as packaging, and the materials contained within the packaging are oily or greasy. For aesthetic reasons, for example, a paper substrate should be resistant to oil and grease stains and "stain proof." Stain resistant materials can either be provided  
20    by the presence of a physical barrier or an oil and grease repellent material, e.g., fluorocarbons. Where only a repellent material is used, the oil and grease can pass or bleed through a fiber matrix within the substrate without showing a stain on the paper material, but staining of surfaces outside of the paper material can occur. If a physical barrier also is used, however, staining of external paper surfaces are generally  
25    prevented. This stain proof requirement exists in manufacturing, packing, shipping and handling environments. Many times the stain proof substrate is the outer print ply of the paper.

[0003] For years, most oil and grease resistant coatings for paper products contained chemicals known as fluorocarbons. These fluorocarbon-based coatings often are saturants applied by paper machines. An example of this type of coating having some fluorocarbon content is described in U.S. Pat. No. 5,674,961 by Fitzgerald titled "Oil  
5 Water And Solvent Resistant Paper By Treatment With Fluorochemical Copolymers" ("the '961 patent"). Synthetic fluorocarbons, however, have recently come under governmental and environmental group scrutiny due to their alleged potential deleterious environmental effects.

[0004] Prior attempts have been made to decrease the environmental effects of  
10 fluorocarbons. Alternative synthetic fluorocarbon paper treatments with more environmentally friendly characteristics have been developed. Problems still exist with these alternatives, however. For example, many of the alternatives such as described in the '961 patent still contain fluorocarbon content. Additionally, these fluorocarbon alternatives can be expensive to produce, and it is uncertain if a reliable  
15 supply source exists for the future.

[0005] One example of an attempt for a more environmentally friendly oil and grease resistant compound is described in U.S. Pat. No. 4,097,297 by Keene titled "Barrier Coatings" ("the '297 patent") The '297 patent describes an overprint varnish that is nitrocellulose based. Applicants have recognized, however, that problems still exist  
20 with this alternative. The overprint varnish, for example, still contains fluorocarbons in a small percentage in its composition. This overprint varnish works better when used in a solution containing a solvent. The use of a solvent, however, adds considerable costs to the manufacturing process and the solvents may emit harmful volatile organic chemicals "VOC's" during application. Additionally, the method of  
25 drying the overprint varnish to substrates is inefficient and time-consuming. The drying process requires drying either with a heater, which increases capital costs, or at room temperature, which increases the time required to dry the overprint varnish.

[0006] It has been suggested that other natural compounds, such as starch compounds, can be used as extenders or additives in oil and grease resistant coatings  
30 to reduce the level of fluorocarbons required in the coating for use in paper product

applications such as packaging. Examples of such starch-based materials can be found in U.S. Patent No. 6,528,088 titled "Highly Flexible Starch-Based Films" ("the '088 patent") and U.S. Patent No. 6,375,981 titled "Modified Starch As A Replacement For Gelatin In Soft Gel Films And Capsules" ("the '981 patent"), both  
5 by Gillenland et al. The performance of these materials for paper product applications, however, has been marginal. Applicants have recognized that these starch-based materials are too brittle for use as a fluorocarbon extender in forming primary oil and grease resistant compounds for many paper product applications because the coating and paper product would be inflexible and would tend to crack or  
10 crease when shaped or formed. Additionally, because such fluorocarbon extender coatings tend to have relatively high viscosity, using such starch-based derivatives as an extender coating can cause difficulties when the coating is used in various paper-related applications. For example, the typical conventional printing machinery that is used to apply the starch materials to the substrates cannot handle certain amounts of  
15 gel in the paper products. Gel formation is necessary, however, in the previously proposed fluorocarbon extender starch-based compounds to achieve the level of solids concentration required for sufficient oil and grease resistance properties. Because of the level of gel formation, the printing machinery cannot handle the high solids concentration within the starch material, and unsightly bubbles can form in the  
20 coating. As a result of these problems recognized by Applicants, the proposed use of starch-based compounds as extenders to reduce the level of fluorocarbons required in the coating is limited. Additionally, the environmental concerns inherent with the presence of fluorocarbons still remain when the starch-based compound is used as an extender.

25 [0007] In addition to the oil and grease resistance requirements, Applicants have recognized previously proposed fluorocarbon-extender alternative starch-containing paper product treatment materials have not shown other additional features that are sometimes desired, such as the capability for use in high temperature applications like packaging for microwave popcorn bags, microwavable food wrappers, and the like.  
30 U.S. Patent No. 5,488,220 by Freerks et al. titled "Bag For Microwave Cooking," U.S. Patent No. 5,038,009 by Babbitt titled "Printed Microwave Susceptor And Packaging

Containing The Susceptor," and U.S. Patent No. 5,171,594 by Babbitt titled "Microwave Food Package With Printed-On Susceptor" all contain examples of paper products used in packaging for high temperature applications, specifically microwave oven applications. Previously proposed fluorocarbon-alternative starch-containing paper product treatment materials, however, have shown minimal scorch resistance and tended to turn brown at higher temperatures.

[0008] Various other non-fluorocarbon alternatives have been developed to combat the environmental and other consequences of using fluorocarbons. Such developments include synthetic latexes, a combination of natural cellulosic gums, starch, and/or proteins, and heavy paper refining. Although these alternatives may be more environmentally friendly than fluorocarbons, there are still problems using these alternatives. The use of synthetic latexes or the combination of natural cellulosic gums, starch, and/or proteins requires very high coat weights when applying them to the paper substrates. The high coat weights result in poor paper machinery operation and increase the amount of maintenance required on these machines. Each of the alternatives is very costly, which makes them economically infeasible. Additionally, none of the three alternatives provide very good oil and grease resistance.

[0009] Most producers of paper products purchase paper substrates that are pretreated with oil and grease resistant materials, such as those described above. The producers apply their graphics to the pretreated substrates, apply an overprint varnish over the graphics, and then form their end products. This increases the raw material costs for these producers, since oil and grease resistant coatings increase the cost of the paper substrates.

[0010] Applicants recognized that a need still exists for a paper product that is environmentally friendly and provides superior barrier properties to oil and grease. With increased market competition, the paper product preferably needs to be able to be decorated aesthetically and possess enough strength to withstand the elements to which the paper product will be exposed. Applicants also recognized that a further need exists for a type of paper product that can provide needed oil and grease resistant properties, along with being able to perform well in high temperature applications and

be sufficiently scorch resistant. Applicants further recognized that a need exists for a type of paper product that is sufficiently flexible and uses a coating that has a relatively low viscosity so that the coating can be effectively applied to various types of paper.

5

### SUMMARY OF THE INVENTION

[0011] With the foregoing in mind, embodiments of the present invention advantageously provide a method for forming a non-fluorocarbon treated substrate having oil and grease resistant properties and related substrates. Embodiments of the present invention also advantageously provide a non-fluorocarbon treated substrate  
10 that has oil and grease resistant properties and is environmentally friendly and relatively economical to produce. Also, the substrate and method according to embodiments of the present invention advantageously provide a substrate with coating that gives increased flexibility and resistance to cracking. The substrate and method according to embodiments of the present invention additionally provide a substrate  
15 with a coating that is advantageously lower in viscosity, which increases compatibility with typical paper making equipment. Also, the substrate and method according to embodiments of the present invention further provide a substrate with a coating that is advantageously resistant to browning and scorching at increased temperatures.

[0012] More particularly, a method of forming a non-fluorocarbon treated substrate  
20 having oil and grease resistant properties is provided according to embodiments of the present invention and includes supplying a starch-based coating comprising a pre-selected percent by weight of at least one pre-selected starch derivative, a flexibility enhancing agent, and a rheological agent. The at least one pre-selected starch derivative includes a chemically modified starch. The method also includes adding  
25 water to the starch-based coating and heating the starch-based film to form a starch solution. The method also includes applying the starch solution to overlie and abuttingly contact a substrate comprising a paper material and thermally curing the starch solution on the substrate thereby forming a starch-based film on the substrate.

[0013] An embodiment of the present invention also provides a non-fluorocarbon  
30 treated substrate including a paper material. The substrate has a starch film overlying

and abuttingly contacting the substrate. The starch film can include a starch-based film. The starch-based film can have a pre-selected percent by weight of at least one pre-selected starch derivative, a flexibility enhancing agent, and a rheological agent. The at least one starch derivative can include a chemically modified starch. The  
5 substrate can also include a starch solution having a clay material further having hydrated silicates of aluminum such as when the substrate, e.g., a paper material, is used in low temperature applications such as in pet food or charcoal packaging. Alternatively, the starch solution can include a scorch resistant agent when the substrate is used in high temperature applications such as microwave packaging. The  
10 substrate can further include printing indicia on the starch-based film. The coating can be applied by using a puddle press, a meter size press, blade coating, roll coating, rod coating, and rotogravure.

[0014] The grease resistant coating on the substrate(s) can be supplied in a composition having a solids concentration by weight of about 10 % to about 35 % and  
15 preferably substantially free from a gel formation. The coating preferably has a viscosity in a range of about 65 centipoises to about 156 centipoises, and the solids concentration by weight, even more preferably, is about 20% to about 25%.

[0015] Embodiments of the non-fluorocarbon treated substrate, e.g., a paper material, and methods for producing a non-fluorocarbon treated paper that have oil and grease  
20 resistant properties and are devoid of fluorocarbons advantageously have significantly reduced brittleness, significantly increased flexibility, and increased resistance to oil and grease staining due to reduced cracking in or around folds in a substrate such as when used in packaging applications. Because an embodiment of a starch-based derivative coating is used for a paper substrate of the present invention, the coating  
25 advantageously can be used with conventional paper making equipment to form substrates of paper material. Also, in addition to the coating being devoid of fluorocarbons, the paper and methods according to embodiments of the present invention can have enhanced scorch resistance properties and enhanced oil and grease resistance characteristics.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0016] Some of the objects and advantages of the present invention having been stated, others will become apparent as the description proceeds when taken in conjunction with the accompanying drawings, in which:

5 [0017] FIG. 1 is a perspective view of a substrate with a starch coating applied to a top surface of the substrate in accordance with an embodiment of the present invention;

[0018] FIG. 2 is a perspective view of a substrate with a starch coating applied to a top surface and a bottom surface of the substrate in accordance with an embodiment  
10 of the present invention;

[0019] FIG. 3A is an enlarged fragmentary sectional view of a substrate taken along line 3 – 3 of FIG. 1 illustrating a starch coating applied to a top surface of the substrate in accordance with another embodiment of the present invention;

[0020] FIG. 3B is an enlarged fragmentary sectional view of a substrate taken along  
15 line 3 – 3 of FIG. 1 illustrating a starch coating having a clay material mixed within the starch coating applied to a top surface of the substrate in accordance with still another embodiment of the present invention;

[0021] FIG. 4A is an enlarged fragmentary sectional view of a substrate taken along  
20 the line 4 – 4 of FIG. 2 illustrating a starch coating applied to a top surface and a bottom surface of the substrate in accordance with another embodiment of the present invention;

[0022] FIG. 4B is an enlarged fragmentary sectional view of a substrate taken along  
25 the line 4 – 4 of FIG. 2 illustrating a starch coating having a clay material mixed within the starch coating applied to a top surface and a bottom surface of the substrate in accordance with still another embodiment of the present invention;

[0023] FIG. 5 is a perspective view of a apparatus for forming a substrate with increased oil and grease resistance and devoid of fluorocarbons in accordance with an embodiment of the present invention;

5 [0024] FIG. 6A is a simplified block flow diagram of a process for forming a substrate including a scorch resistant agent having oil and grease resistant properties according to an embodiment of the present invention;

[0025] FIG. 6B is a simplified block flow diagram of a process for forming a substrate including hydrated silicate of aluminum and having oil and grease resistant properties according to an embodiment of the present invention;

10 [0026] FIG. 7 is a table illustrating the effect of increasing a total amount of solids in a starch-based coating material on the elasticity of the coating, which is indicated by an increase in the viscosity of the starch solution, in accordance with an embodiment of the present invention;

15 [0027] FIG. 8 is a graph of the percent of solids versus the viscosity from the table of FIG. 7 illustrating the effect on the elasticity of a starch-based coating, which is shown by an increase in viscosity, with an increase in a total amount of solids in the starch material in accordance with an embodiment of the present invention;

20 [0028] FIG. 9 is a table illustrating the results from felt tests indicating the effect of percent total solids on the flexibility of a starch material in accordance with an embodiment of the present invention;

[0029] FIG. 10 is a graph of percent failure versus time illustrating the results of a flat felt test for a coating as a percent of failure versus time for four different total solids concentrations within the coating in accordance with an embodiment of the present invention;

25 [0030] FIG. 11 is a graph of percent failure versus time illustrating the results of a creased felt test for a coating as a percent of failure versus time for four different total solids concentrations within the coating in accordance with an embodiment of the present invention;

[0031] FIG. 12 is a graph of percent failure versus time illustrating the results of a creased felt test for various coatings having a starch-based derivative with a total solids concentration of 21.1% as a percent of failure versus time for four various coatings in accordance with an embodiment of the present invention;

5 [0032] FIG. 13 is a graph of percent failure versus time illustrating the results of a creased felt test for various coatings having a starch-based derivative with a total solids concentration of 10.5% as a percent of failure versus time for four various coatings in accordance with an embodiment of the present invention;

10 [0033] FIG. 14 is a graph of percent failure versus time illustrating the results of a creased felt test for various coatings having a starch-based derivative with a total solids concentration of 6.57% as a percent of failure versus time for four various coatings in accordance with an embodiment of the present invention;

15 [0034] FIG. 15 is a table illustrating the results from scorch resistance tests for various coatings on two different grades of packaging paper in accordance with an embodiment of the present invention;

[0035] FIG. 16 is a bar graph showing identification number versus scorch resistance ranking for a particular grade of packaging paper, i.e., 21 pounds (#) popcorn grade, containing a coating in accordance with an embodiment of the present invention; and

20 [0036] FIG. 17 is a bar graph showing identification number versus scorch resistance ranking for a particular grade of packaging paper, i.e., 25 pounds (#) popcorn grade, containing a coating in accordance with an embodiment of the present invention.

### DETAILED DESCRIPTION

25 [0037] The present invention now will be described more fully hereinafter with reference to the accompanying drawings in which embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these

embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout. Prime notation where used indicates similar elements in alternative embodiments.

5 [0038] FIGS. 1 and 2 illustrate perspective views of different embodiments of a non-fluorocarbon treated high temperature paper having oil and grease resistant properties, being devoid of fluorocarbons. Being "devoid of fluorocarbons" as used herein means that the coating or other packaging is substantially devoid of fluorocarbons more preferably having no fluorocarbons, or alternatively only minute traces of  
10 fluorocarbons. The paper, as shown in FIG. 1 and corresponding FIGS. 3A and 3B, for example, includes at least one substrate 20 formed of a paper material and having an outer surface 21. A coating 24 can be positioned on an outer surface 21 of the substrate 20. In another embodiment, as shown in FIG. 2 and corresponding FIGS. 4A and 4B, the paper 20' can have a coating 24' positioned on an outer surface 21' of  
15 the substrate 20', and further have another starch-based coating 26 positioned on an inner surface 22' of the substrate 20'.

[0039] The coating 24 advantageously can include, as shown in FIGS. 3B and 4B, a clay material 28, for example, a hydrated silicate of aluminum, to extend the coating 24 and provide an additional physical barrier for increased oil and grease resistance,  
20 as well as provide the final paper product with a smoother outside surface that is, for example, appealing to consumers. The clay material 28 can be mixed with the coating 24, or else layered as understood by those skilled in the art.

[0040] The coating such as shown in FIGS. 2 and 4A-4B preferably includes a starch-based film having a pre-selected percent by weight of at least one pre-selected starch  
25 derivative, a flexibility enhancing agent, a rheological agent, and a scorch resistant agent. The at least one starch derivative preferably is a chemically modified starch. The flexibility enhancing agent is preferably selected from a group consisting of a monomer diluent and a flexible polymer. The monomer diluent is preferably selected from the group consisting of glycols, water, glucose, sucrose, oligosaccharides, and  
30 combinations thereof and the flexible polymer is preferably selected from the group

consisting of ethyl cellulose, carboxymethyl cellulose, derivatized polysaccharides, and combinations thereof. The rheological agent is preferably selected from a group consisting of a solvent, a dispersant, and combinations thereof. The solvent is preferably selected from the group consisting of glycols, water, glucose, sucrose, oligosaccharides, and combinations thereof and the dispersant is preferably selected from the group consisting of linear high molecular weight polysaccharides, ethoxylated saccharides, and combinations thereof. The scorch resistant agent is preferably selected from glycol, a sucrose derivative, a phosphate derivative of sugar, and combinations thereof. The coating also is preferably substantially free of protein.

10 [0041] Examples of starch-based films can be found in U.S. Patent No. 6,528,088 titled "Highly Flexible Starch-Based Films" ("the '088 patent") and U.S. Patent No. 6,375,981 titled "Modified Starch As A Replacement For Gelatin In Soft Gel Films And Capsules" ("the '981 patent"), both by Gillenland et al., and both of which are incorporated herein in their entirety. As understood by those skilled in the art, the starch-based films described in the '088 patent and the '981 patent can be utilized as a starting point, and modified as discussed herein by including a flexibility enhancing agent preferably selected from the group as described herein, a rheological agent preferably selected from the group as described above, and a scorch resistant agent preferably selected from the group as described above, to make and use the starch-based derivative coating devoid of fluorocarbons as described herein

25 [0042] FIG. 7 is a table illustrating the effect of increasing a total amount of solids in a starch material on the elasticity of the starch. Starch derivatives A and B are successive generations or derivations of the starch material. Elasticity is indicated by an increase in the viscosity of the starch solution. As illustrated, when starch is used as an extender, viscosity can increase as the percentage of solids in the starch material increases. This is also shown in the graph of FIG. 8. Additionally, even when viscosity does not increase, starch pickup in pounds per ton and oil and grease resistance, as measured by 3M Kit test results as understood by those skilled in the art, can increase.

[0043] Based on the information from these studies conducted by Applicants, Applicants were able to determine that a starch-based derivative coating can be developed by adding a flexibility enhancing agent and a rheological agent and yet be substantially gel free. Applicants recognized that the existing starch-based derivative can have higher gelling qualities as the concentration of solids is increased. The coating preferably includes a composition having a solids concentration by weight of about 10% to about 35%, more preferably about 20% to about 25%, and is substantially free from a gel formation. The coating preferably has a viscosity in a range of about 65 centipoise to about 156 centipoise. The starch-based material preferably includes at least one starch material including potato starch, cornstarch, and water. Applicants also recognized that coating inner and outer surfaces of substrates can prevent grease, or increase grease holdout, such as generated during cooking or microwave heating of food within a package made of the paper material, from or around a small puncture, fracture, tear, or other opening in an inner surface of a substrate from passing through to another substrate where staining of the other substrate would be more readily viewable by the user such as in packaging applications.

[0044] The table of FIG. 9 illustrates results of a kit test (felt) and RP2, flat and creased, over time in minutes with different percent total solids (“%TS”) by weight, e.g., 6.57%, 10.5%, 21.1%, and 25.3% to 28%. From this data, it can be seen that roughly 100 failures occur after a 24 hour (1440 minutes) period. Nevertheless, up to about 90 minutes or 120 minutes, a starch-based coating having no fluorocarbons closely tracks coatings using a starch-based derivative as a fluorocarbon extender. This significant increase in failure for the 24 hour period as compared to the 2 hour period is shown by the shaded region of the graphs in FIGS. 10-17. This dramatic change and failure of starch-based derivatives as fluorocarbon extenders helped Applicants recognize that a starch-based derivative coating devoid of fluorocarbons can be produced that will significantly decrease the failure rate over time by adding a flexibility enhancing agent and a rheological agent.

[0045] FIG. 15 is a table illustrating the results of a scorch resistance test for various coatings on two different grades of packaging paper, i.e. 21# popcorn grade and 25#

popcorn grade. These results are also graphically illustrated in FIGS. 16 and 17. Applicants recognized that the addition of a scorch resistant agent can significantly reduce the occurrence of browning when a starch-based derivative is used by itself as a coating in high temperature packaging applications.

5 [0046] As illustrated in FIGS. 1-17, and as described herein, methods of forming a non-fluorocarbon treated substrate having oil and grease resistant properties are also included according to embodiments of the present invention. For example, such a method is illustrated in the block diagram of FIG. 6A. As shown in first block 61, the method preferably includes supplying at least one substrate 20 comprising a paper  
10 material having a grease resistant coating 21 devoid of fluorocarbons thereon. The coating 21 preferably is a starch-based film including a pre-selected percent by weight of at least one pre-selected starch derivative, a flexibility enhancing agent, a rheological agent, and a scorch resistant agent. The at least one starch derivative preferably is a chemically modified starch. Water is added to the starch-based coating  
15 21, and the coating 21 is heated to form a starch-based solution. Second block 62 generally show the step of supplying a substrate 20 having coating 21 thereon including the step of applying the coating 21 to one or both surfaces 21, 22 of the substrate 20. The coating 21 can be applied using an application method selected from the group consisting of a meter size press, blade coating, roll coating, rod  
20 coating, and rotogravure, as understood by those skilled in the art. Third block 63 shows the step of thermally curing the coating 21 onto substrate 20 to dry off excess moisture, which can be accomplished by using standard paper machine drying or equipment such as pressurized steam cylinders or dryer cans as understood by those skilled in the art. An alternative embodiment as shown in block 65 of FIG. 6B shows  
25 the additional step of adding a clay material 28, for example, a hydrated silicate of aluminum, to the coating 24 before the coating 24 is thermally cured.

[0047] FIG. 5 shows an embodiment of an apparatus for paper-making according to the present invention. Substrate 20 is passed along a conveyer belt 30, and coating 24 from coating applicator 32 is applied to outer surface 21 of the substrate 20 at press  
30 layer 34 of press roll 35. In an alternative embodiment, coating 24 from coating applicator 32 can be applied to the outer surface 21 of the substrate 20 and to the inner

surface 22 of the substrate 20 at press layer 34 of press roll 35. The resulting material 36 is then thermally cured at dryer 38. The thermal curing can be accomplished by heating ovens, radiant light, or various other methods understood by those skilled in the art. The resulting material 40 can then be utilized by the manufacturer for desired  
5 purposes.

[0048] In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for the purpose of limitation, the scope of the invention being set forth in the following claims.

**THAT CLAIMED IS:**

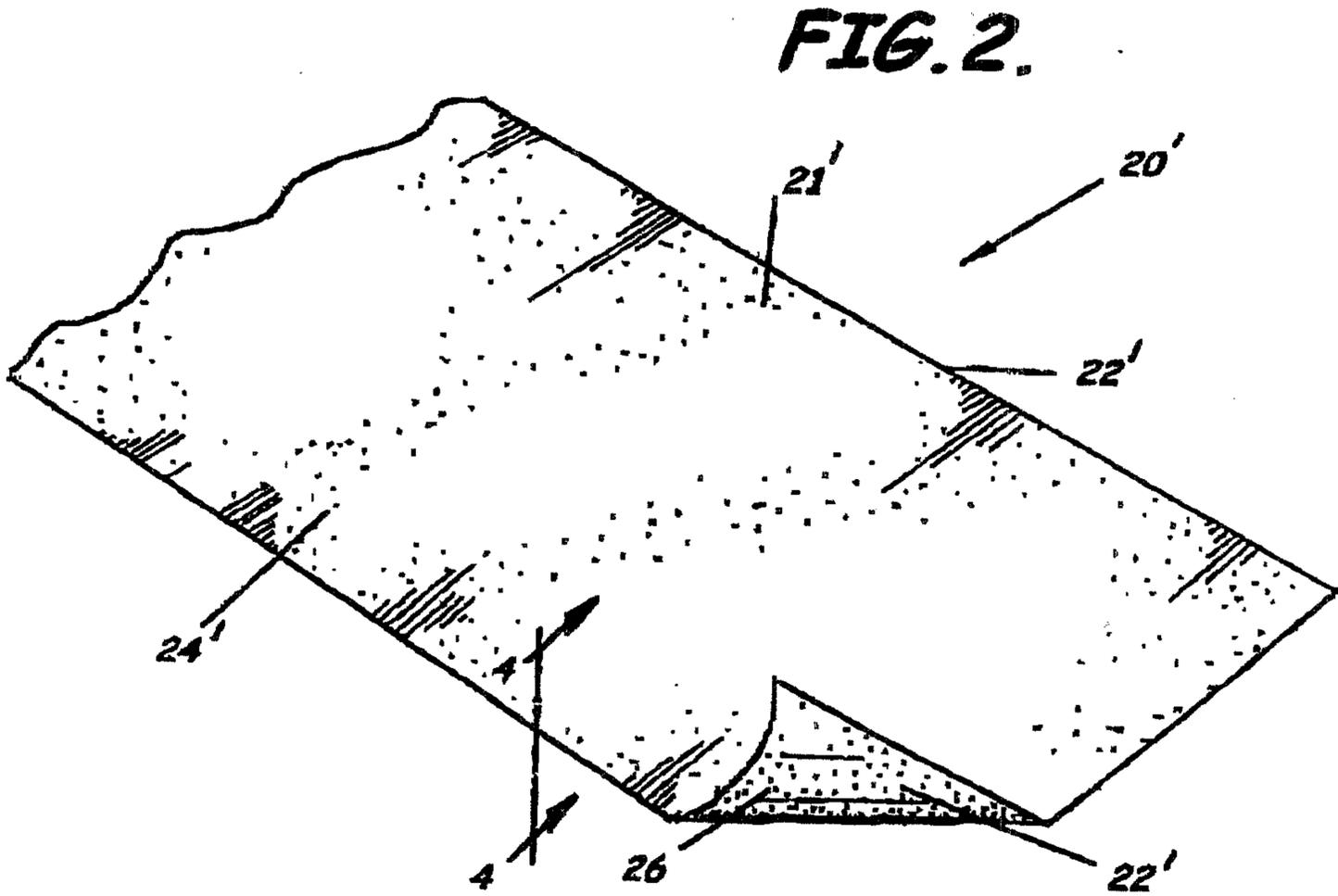
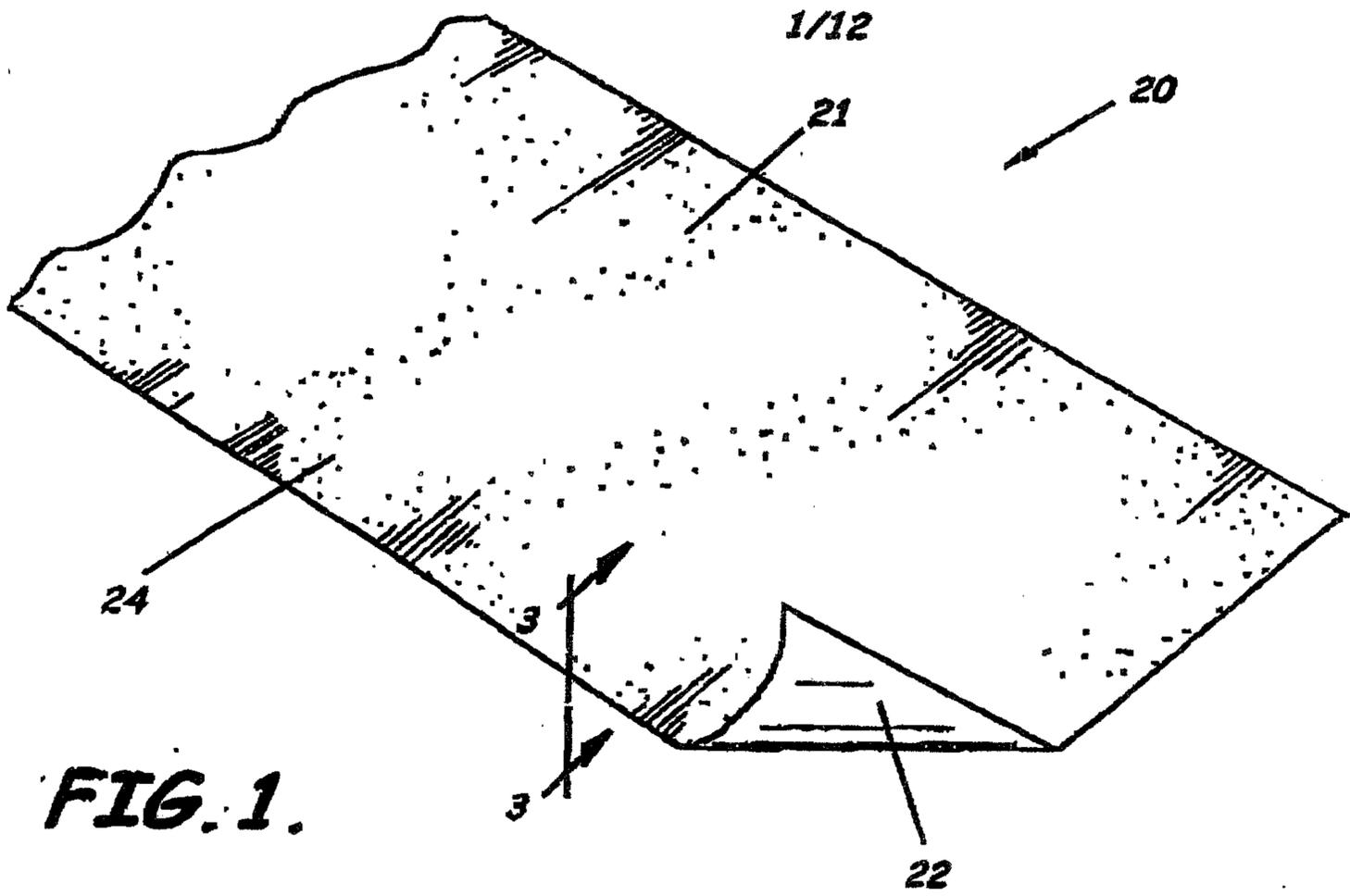
1. A method of forming a non-fluorocarbon treated substrate having oil and grease resistant properties, the method comprising the steps of:
  - 5 (a) supplying a starch-based coating comprising a pre-selected percent by weight of at least one pre-selected starch derivative, a flexibility enhancing agent, and a rheological agent, the at least one pre-selected starch derivative comprising a chemically modified starch;
  - (b) adding water to the starch-based coating;
  - (c) heating the starch-based film to form a starch solution;
  - 10 (d) applying the starch solution to overlie and abuttingly contact a substrate comprising a paper material; and
  - (e) drying the starch solution on the substrate thereby forming a starch-based film on the substrate.
2. A method as defined in claim 1, wherein the flexibility enhancing agent is  
15 selected from a group consisting of a monomer diluent and a flexible polymer.
3. A method as defined in claim 2, wherein the monomer diluent is selected from the group consisting of glycols, water, glucose, sucrose, oligosaccharides, and combinations thereof and the flexible polymer is selected from the group consisting of ethyl cellulose, carboxymethyl cellulose,  
20 derivatized polysaccharides, and combinations thereof.
4. A method as defined in claim 1, wherein the rheological agent is selected from a group consisting of a solvent and a dispersant.
5. A method as defined in claim 4, wherein the solvent is selected from the group consisting of glycols, water, glucose, sucrose,  
25 oligosaccharides, and combinations thereof and the dispersant is selected from the group consisting of linear high molecular weight polysaccharides, ethoxylated saccharides, and combinations thereof.

6. A method as defined in claim 1, further including shaping the starch film into a package.
7. A method as defined in claim 6, further including positioning a food within the package.
- 5 8. A method as defined in claim 1, wherein the starch solution further includes a clay material comprising hydrated silicates of aluminum.
9. A method as defined in claim 1, further including printing indicia on the starch-based film.
- 10 10. A method as defined in claim 1, wherein the coating is substantially free of protein.
11. A method as defined in claim 1, further comprising supplying the coating in a composition, the composition being prepared with water, and wherein the composition has a solids concentration by weight of about 10 % to about 35 %.
12. A method as defined in claim 11, wherein  
15 the coating is substantially free from a gel formation.
13. A method as defined in claim 12, wherein the coating has a viscosity in a range of about 65 centipoises to about 156 centipoises, and wherein the solids concentration by weight is about 20% to about 25%.
14. A method as defined in claim 1, wherein the starch material comprises at least  
20 one of a potato starch, a cornstarch, and water.
15. A method as defined in claim 1, wherein the step of applying the starch solution comprises applying the starch solution by an application method selected from the group consisting of utilizing a meter size press, blade coating, roll coating, rod coating, and rotogravure.
- 25 16. A method as defined in claim 1, wherein the step of drying the starch solution on the substrate includes using an electron beam.

17. A non-fluorocarbon treated substrate comprising a substrate comprising a paper material, the substrate having a starch film overlying and abuttingly contacting the substrate, the starch film comprising a starch-based film, the starch-based film comprising a pre-selected percent by weight of at least one pre-selected starch derivative, a flexibility enhancing agent, and a rheological agent, the at least one pre-selected starch derivative comprising a chemically modified starch.
18. A substrate as defined in claim 17, wherein the flexibility enhancing agent is selected from a group consisting of a monomer diluent and a flexible polymer.
19. A substrate as defined in claim 17, wherein the rheological agent is selected from a group consisting of a solvent and a dispersant.
20. A substrate as defined in claim 17, wherein the coating is substantially free of protein.
21. A substrate as defined in claim 17, further comprising supplying the coating in a composition, the composition being prepared with water, and wherein the composition has a solids concentration by weight of about 10 % to about 25 %.
22. A substrate as defined in claim 21, wherein the coating is substantially free from a gel formation.
23. A substrate as defined in claim 22, wherein the coating has a viscosity in a range of about 65 centipoises to about 156 centipoises.
24. A substrate as defined in claim 17, wherein the starch material comprises at least one of a potato starch and a cornstarch.
25. A substrate as defined in claim 17, wherein the composition is gelatin free.
26. A substrate as defined in claim 17, wherein the step of applying the coating comprises applying the coating by an application package selected from the group consisting of utilizing a meter size press, blade coating, roll coating, rod coating, and rotogravure.

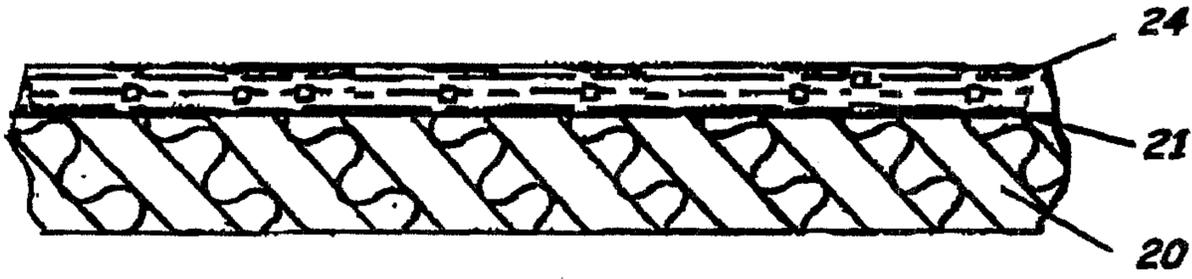
27. A package formed with a substrate comprising a paper material, the substrate having a starch film overlying and abuttingly contacting the substrate, the starch film comprising a starch-based film, the starch-based film comprising a pre-selected percent by weight of at least one pre-selected starch derivative, a flexibility enhancing agent, and a rheological agent, the at least one starch derivative comprising a chemically modified starch.

28. A package as defined in claim 27, wherein the starch film further includes a clay material comprising hydrated silicates of aluminum.

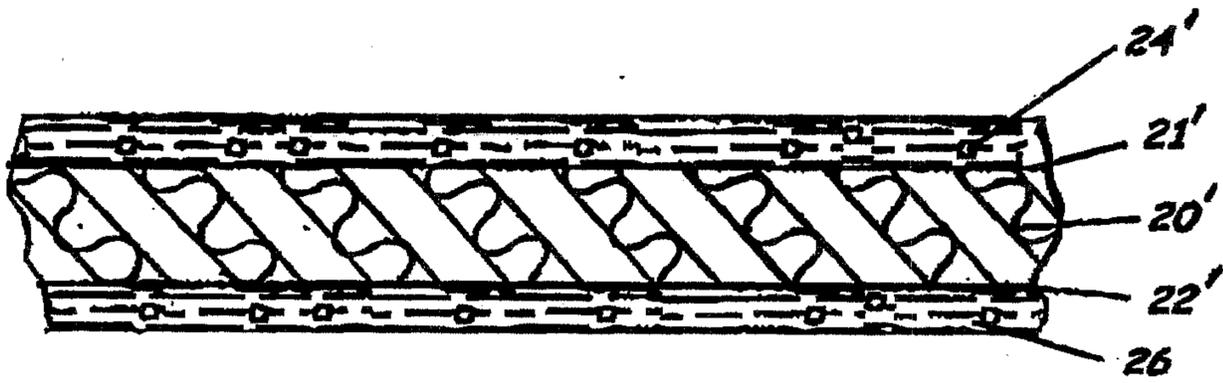


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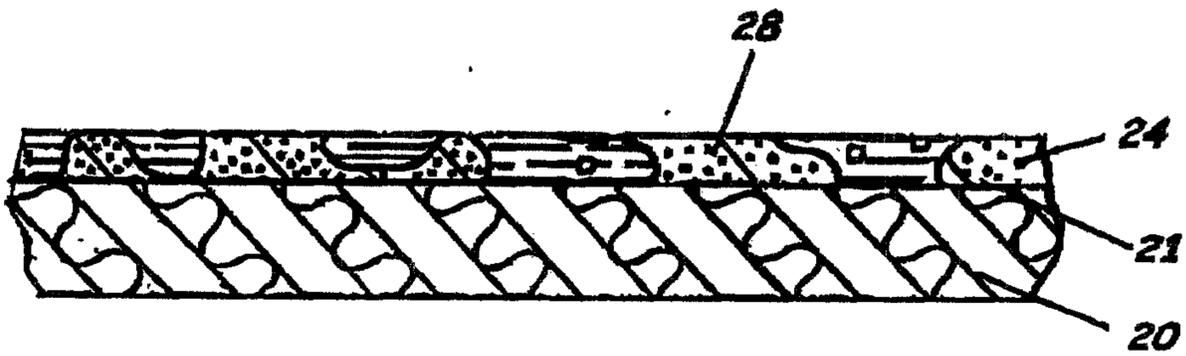
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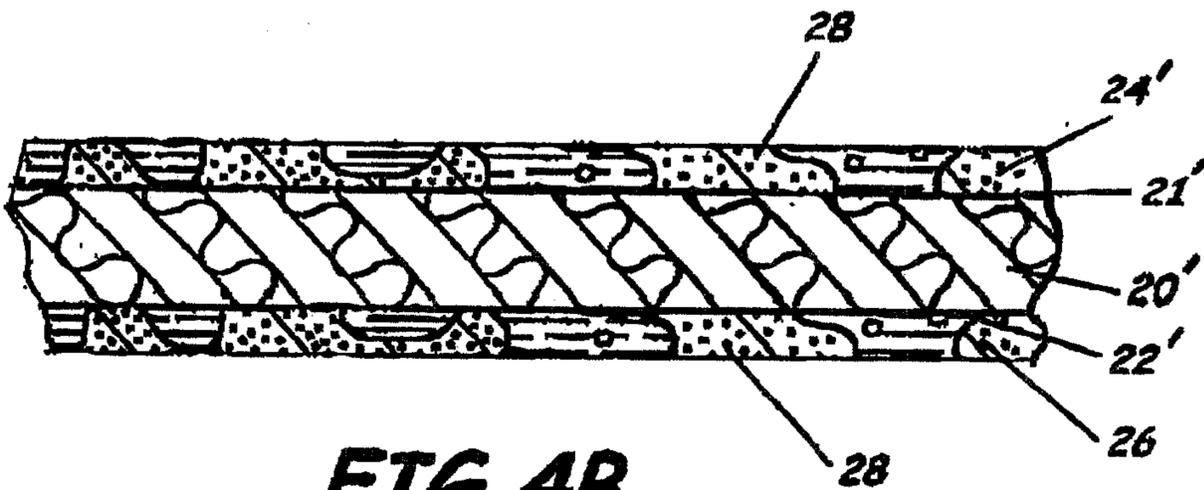
**FIG. 3A.**



**FIG. 4A.**



**FIG. 3B.**



**FIG. 4B.**

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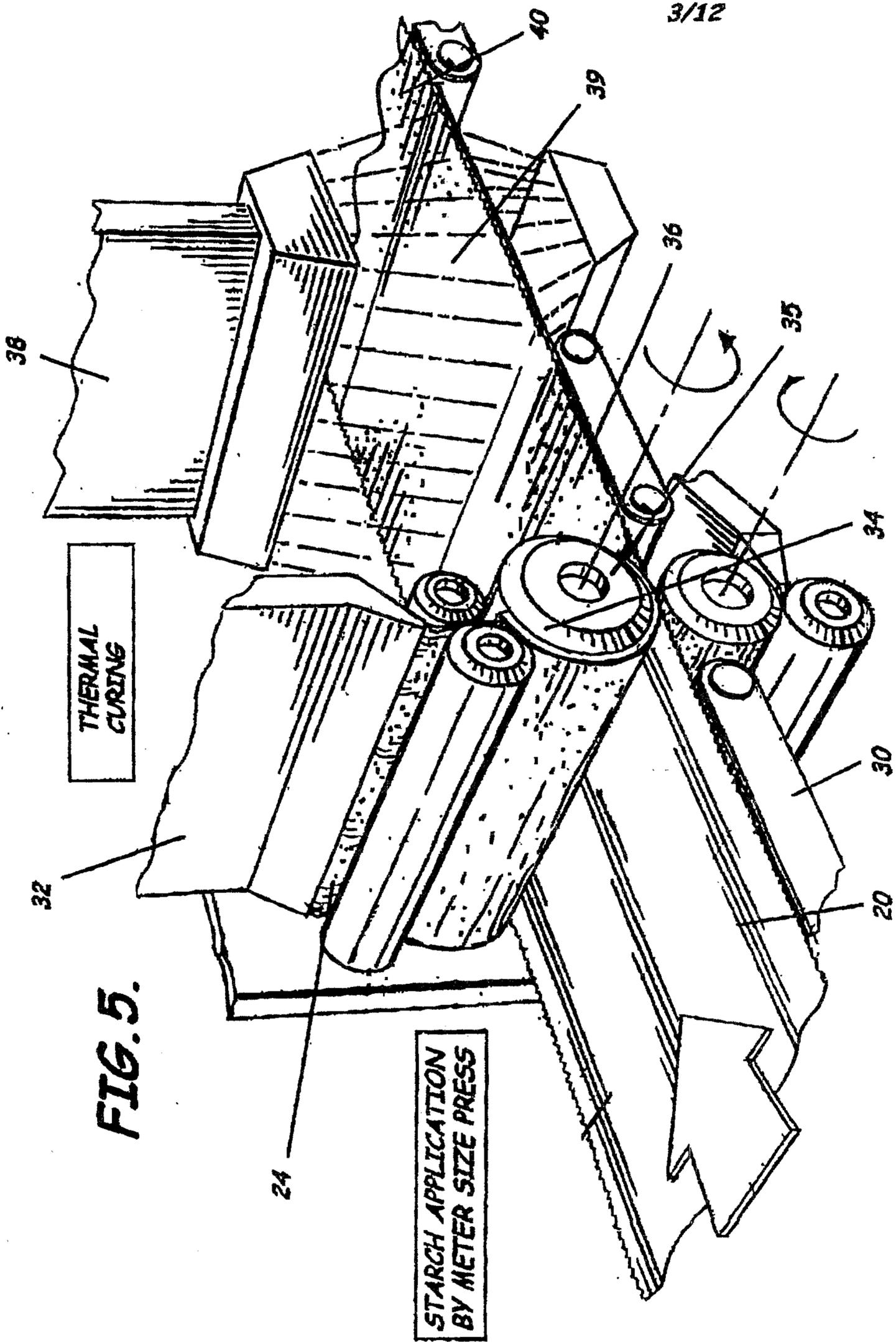
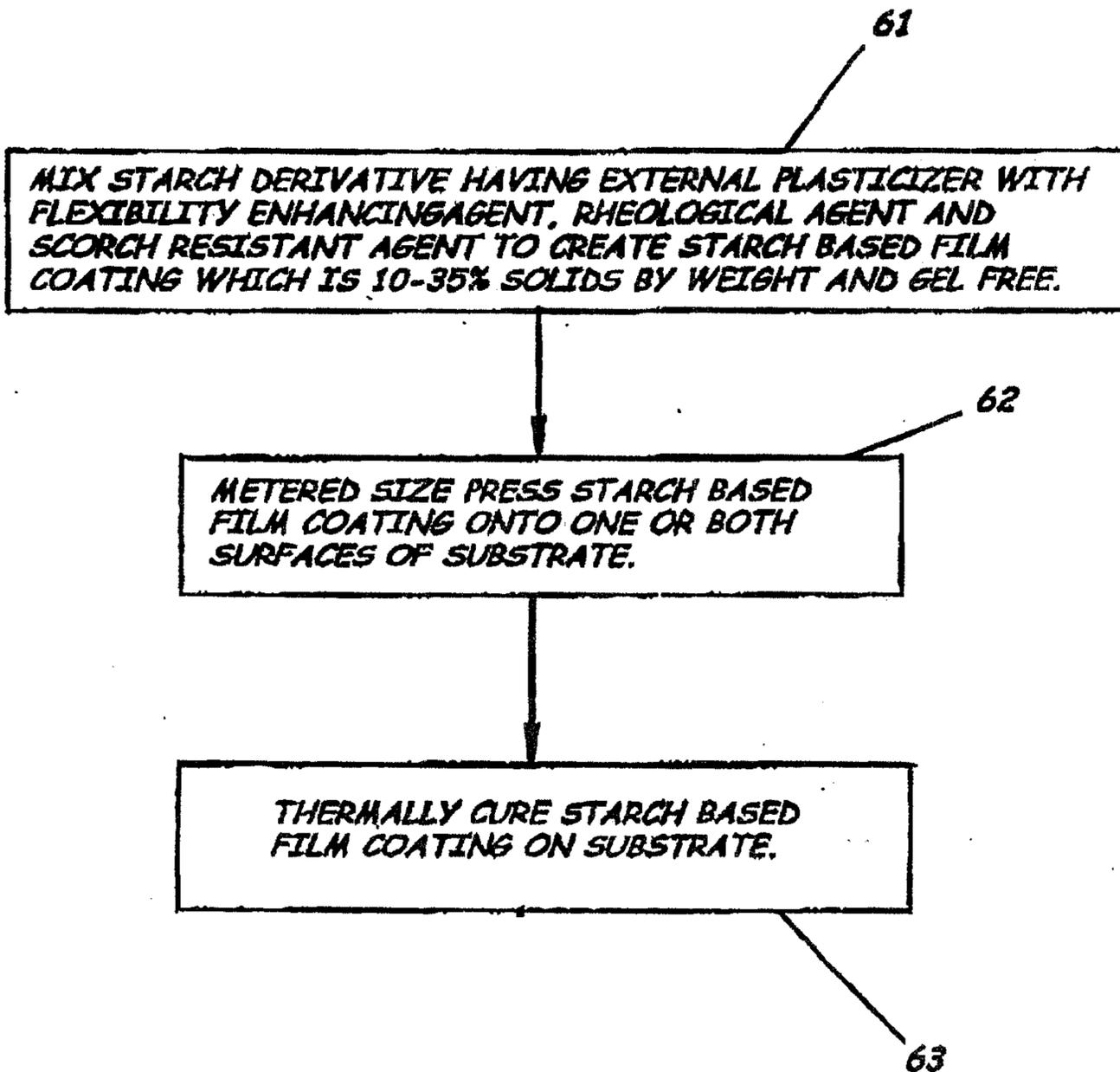


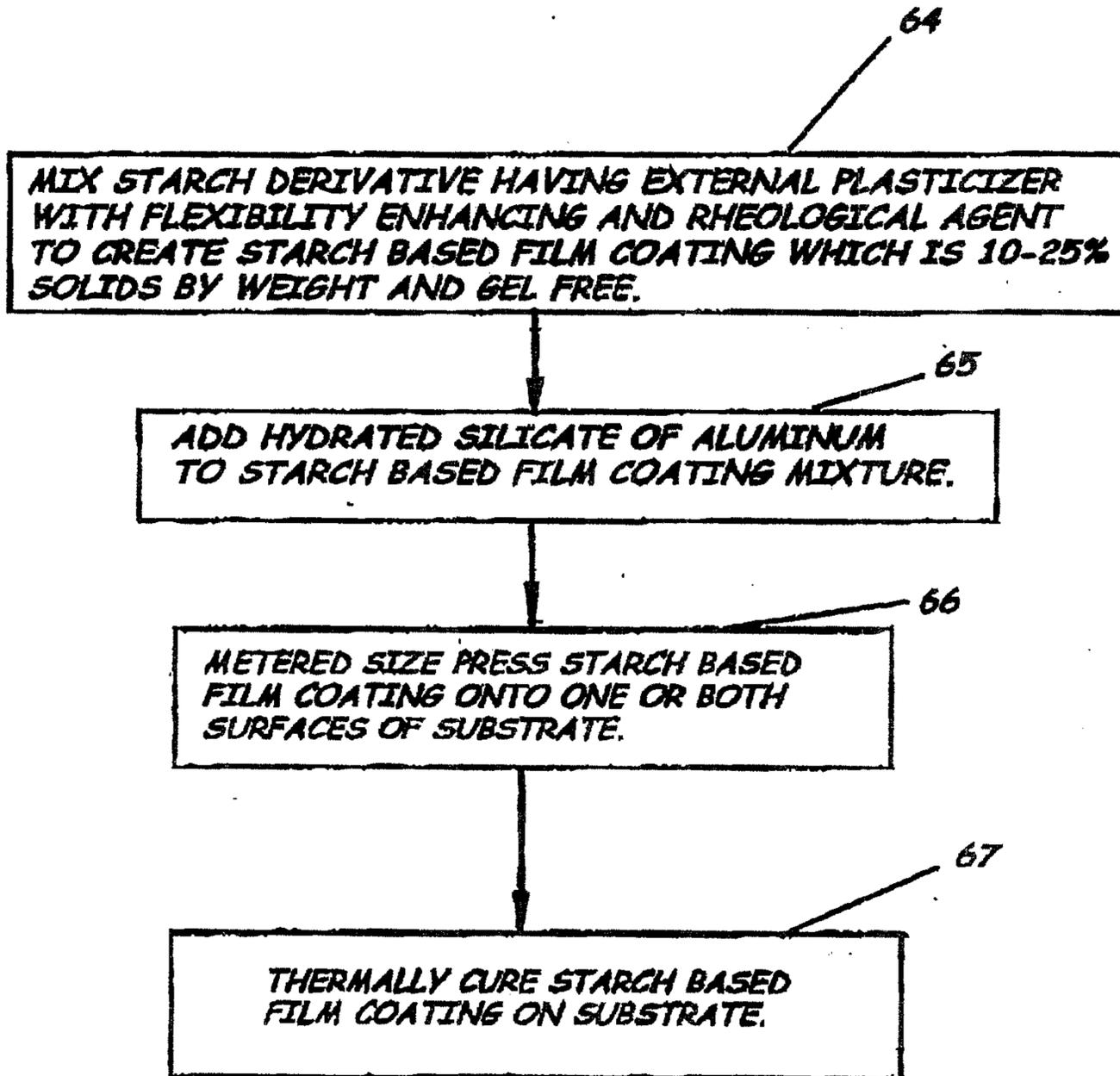
FIG. 5.

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**FIG. 6A.**

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**FIG. 6B.**

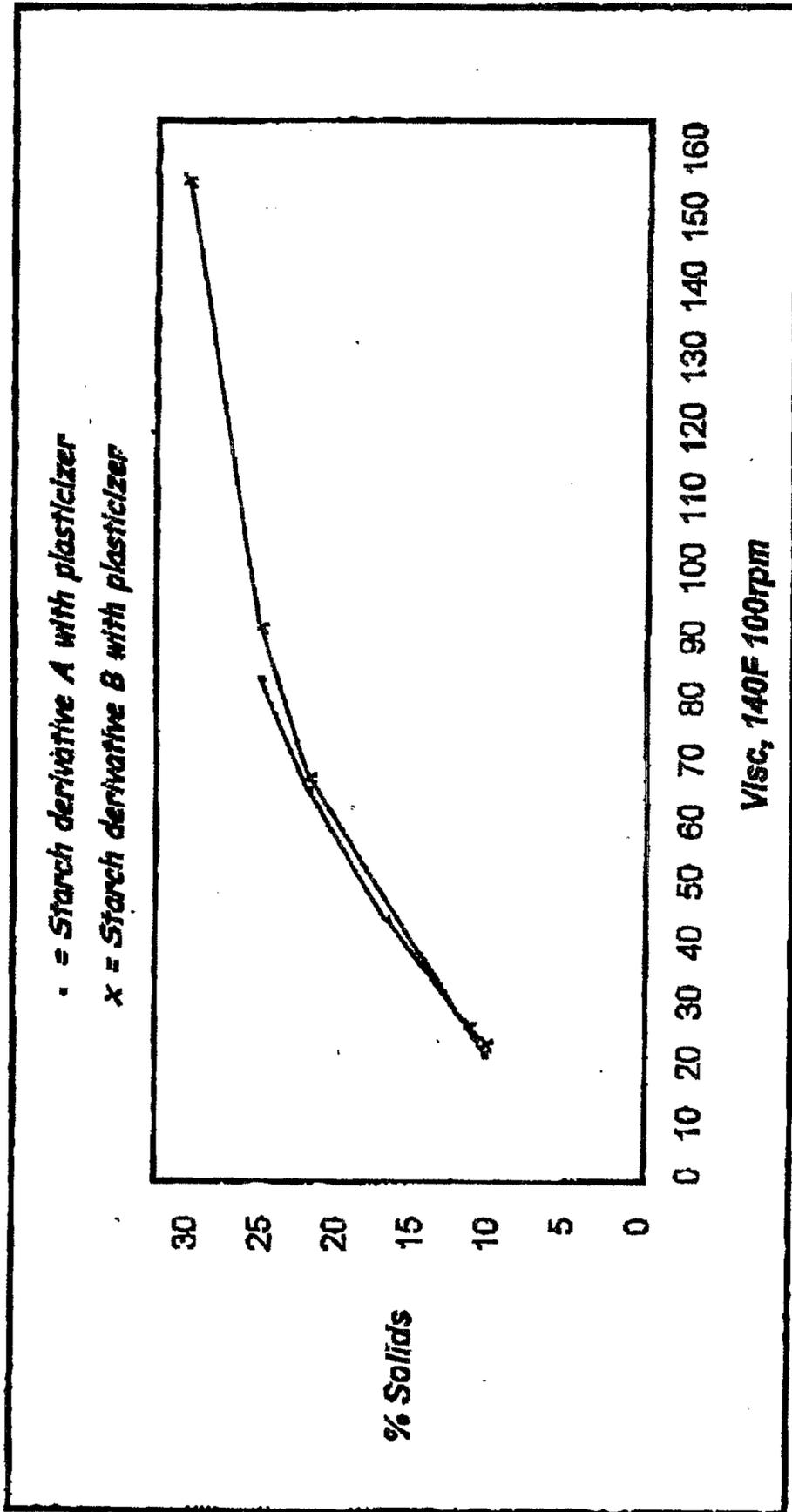
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starch pickup #/ton	Starch derivative with plasticizer	% Solids	V <sub>h</sub> , 140F 100 rpm	IM Test Kit Value
153	A	10	21	3
154	A	10	21	3
165	A	10	21	5
170	A	12	26	5
176	A	10	21	6
243	A	17	42	6
252	A	17	42	9
301	A	17	42	7
308	A	22	65	12
398	A	25	82	12
141	B	10	22	5
160	B	12	26	7
225	B	10	22	7
337	B	22	68	10
359	B	25	91	12
366	B	22	68	12
384	B	25	90	10
416	B	25	90	12
427	B	22	68	9
527	B	30	156	12

FIG. 7.

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**FIG. 8.**





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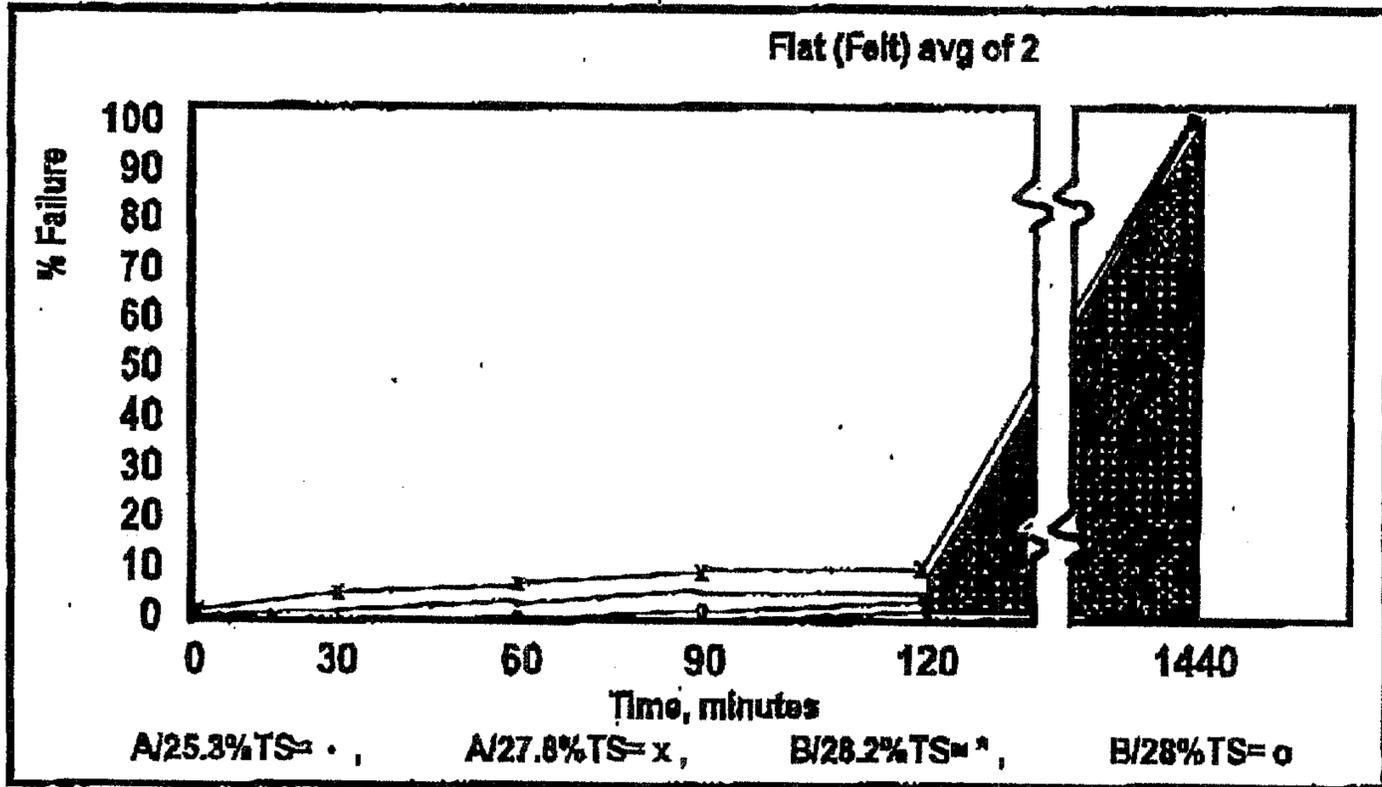


FIG. 10.

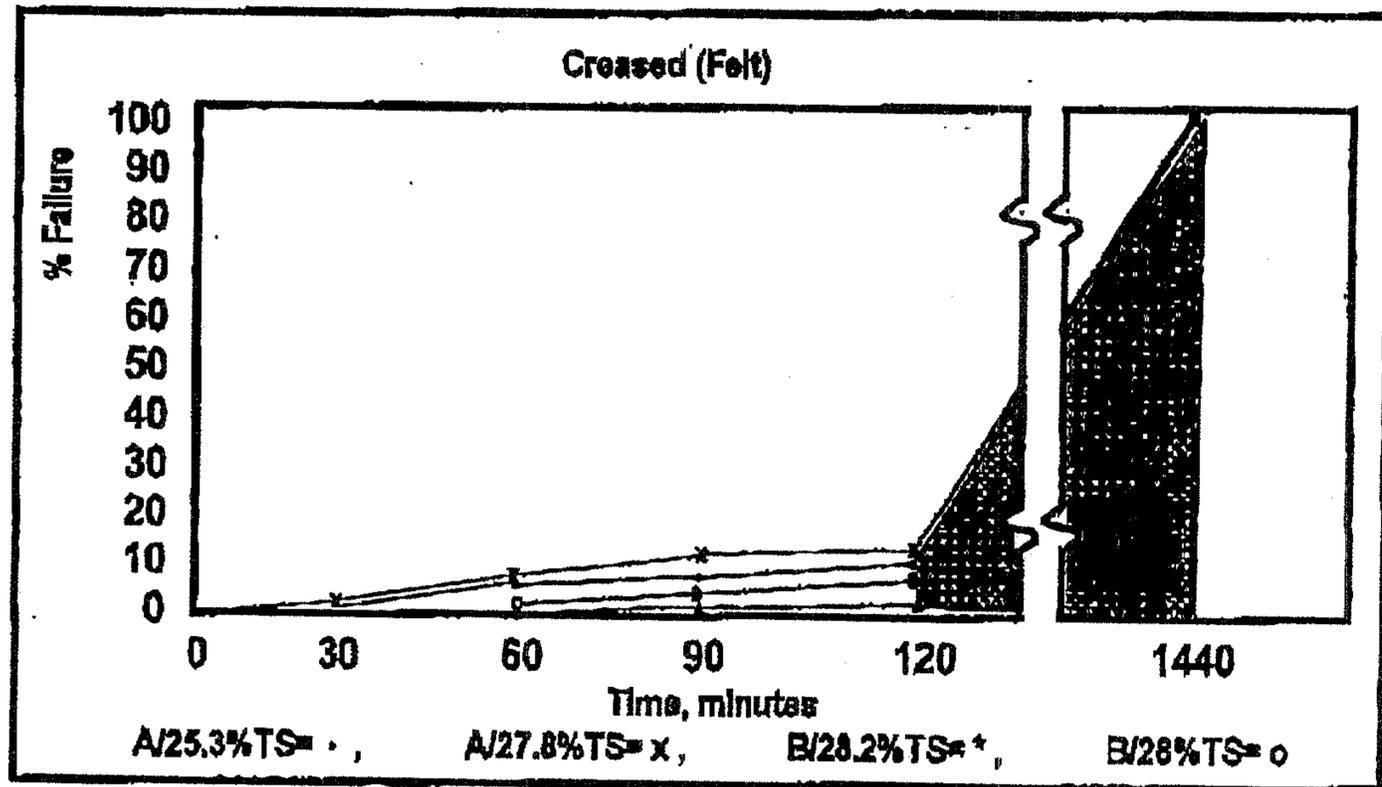


FIG. 11.

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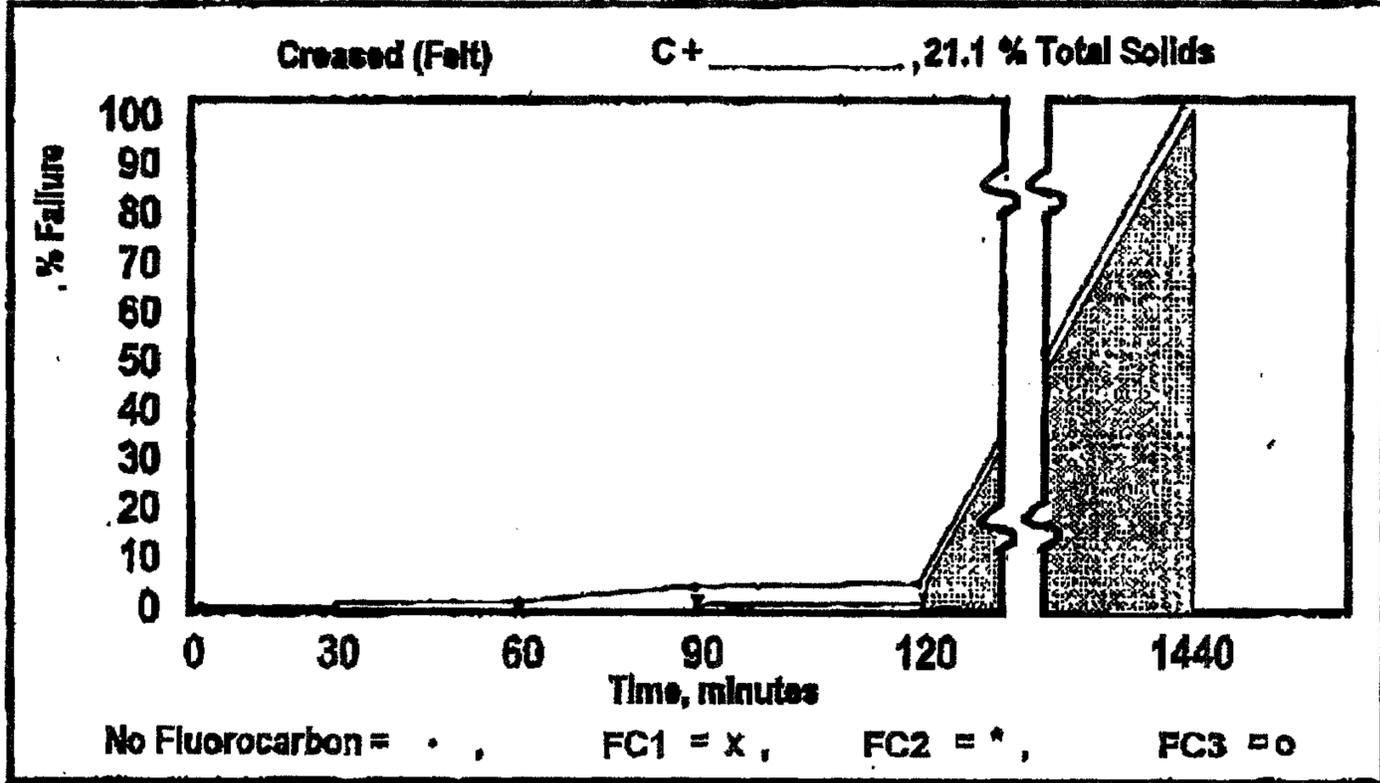


FIG. 12.

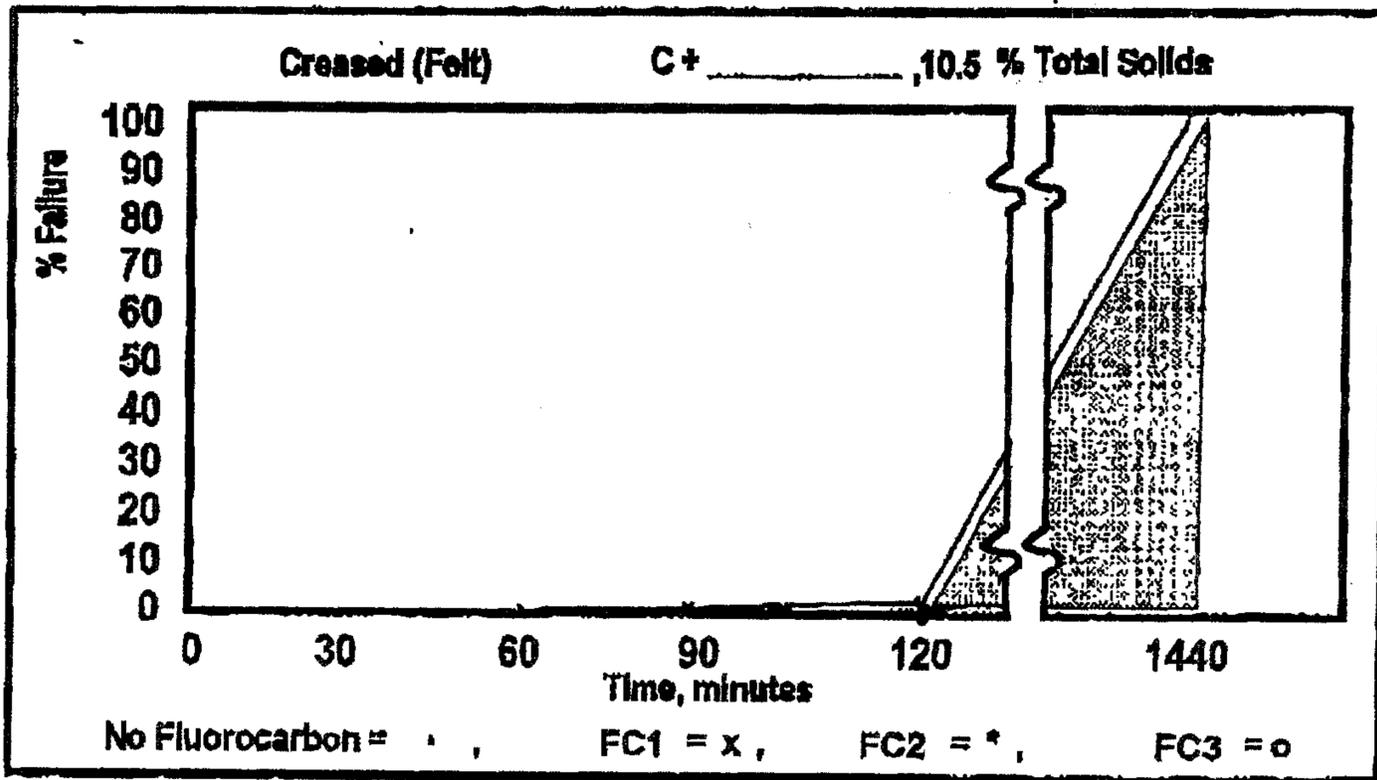


FIG. 13.

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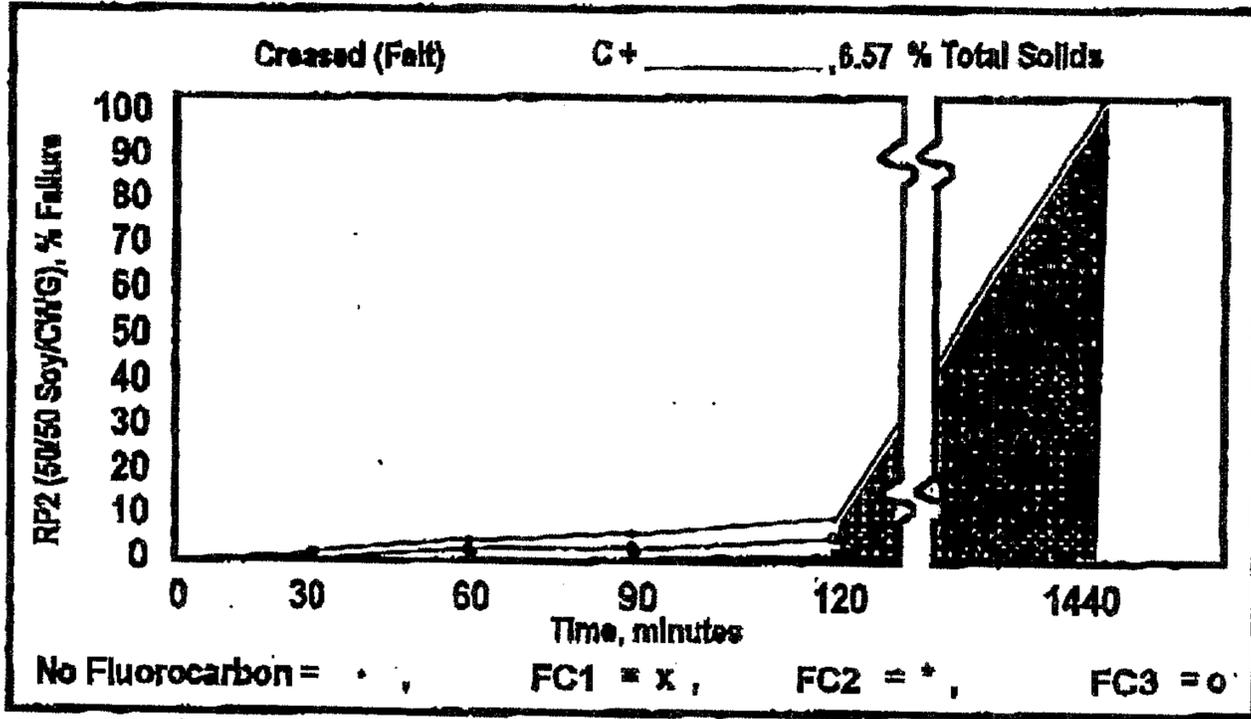


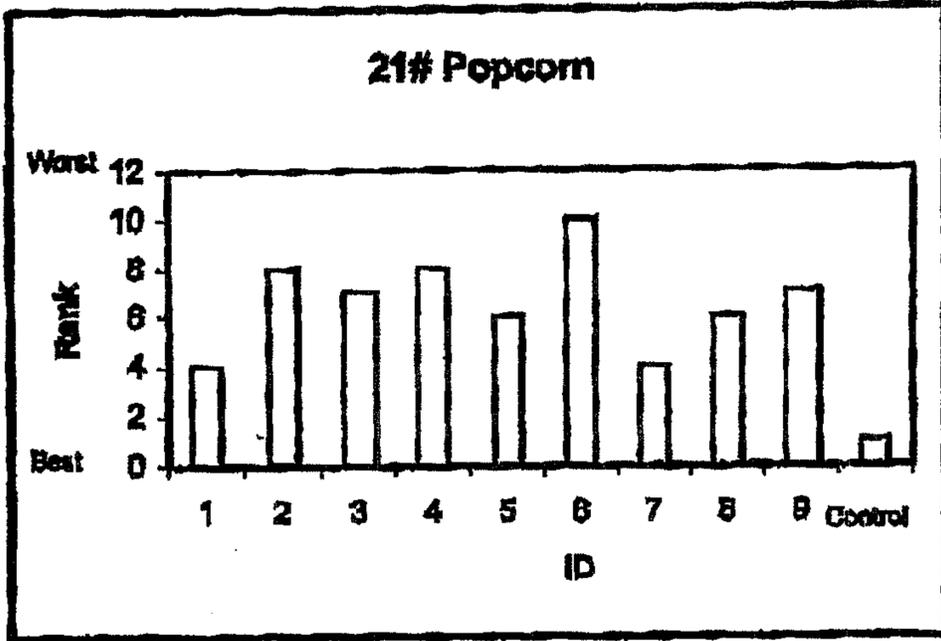
FIG. 14.

ID	BW	CW		30 sec Scorch
		Coating	#ream	
1	21	A	7.1	4
2	21	A	14.6	8
3	21	A	14.7	7
4	21	B	7.4	8
5	21	B	9.8	8
6	21	B	11.4	10
7	21	C	7	4
8	21	C	10.9	6
9	21	C	12.6	7
-	21	control	-	1
10	25	A	11.1	3
11	25	A	16.2	4
12	25	A	17.5	5
13	25	B	11.7	3
14	25	B	12.8	6
15	25	C	6.5	2
16	25	C	10.9	1
17	25	C	13.2	2
-	25	control	-	1

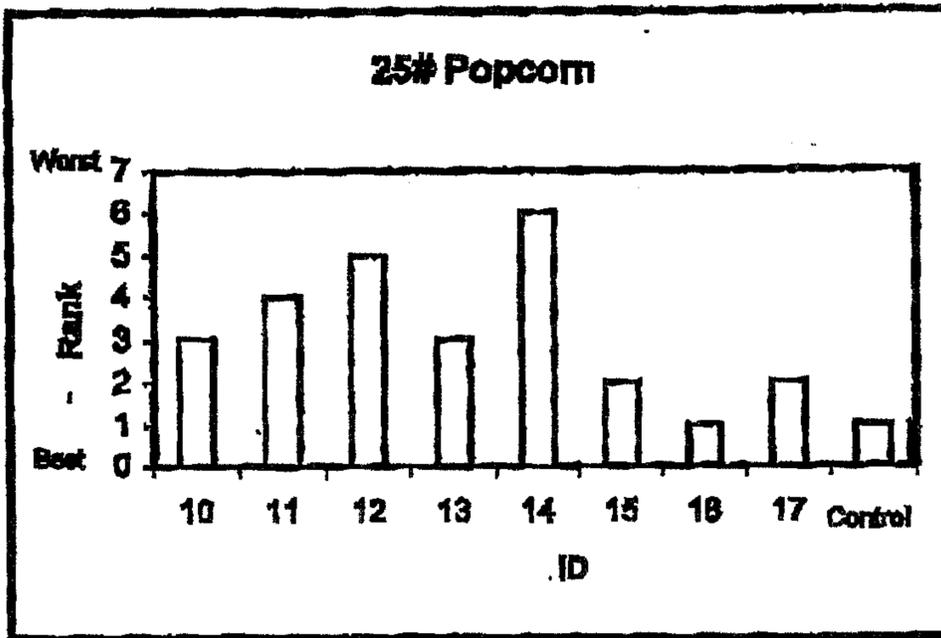
FIG. 15.

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**FIG. 16.**



**FIG. 17.**

