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COATED FLEXIBLE SHEET

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This invention is concerned with producing flexible sheets having adherent protective coatings and contemplates in particular the production of novel lacquered papers.

In producing lacquered papers and the like, it is necessary that the dried lacquer film be strongly adherent, flexible, and non-tacky. Preferably the film should be thermoplastic. It is also desirable that this film be formed from a lacquer in which the proportion of film forming ingredients is relatively high and the proportion of volatile solvents relatively low so that an economy in the use of solvents is enjoyed. Lastly, it is desirable that the lacquer employed contain a relatively large proportion of film forming ingredients at the same time being sufficiently fluid to permit the production of a thick smooth dried film in a single application.

As a result of my investigations I have found that excellent lacquered papers and the like can be produced by employing nitrostarch as the principal and preferably substantially the sole base for the lacquer. Nitrostarch films tend to be both weak and brittle. I have found that the weakness of nitrostarch films used for coating flexible sheets is relatively unimportant so long as brittleness is overcome. Nitrostarch films containing a sufficient amount of plasticizer are very strongly adherent. In fact, such films adhere so strongly to backings such as paper, rubber sheets and the like, that film and backing act almost as a unitary mass, the high tensile strength of the backing being sufficient to compensate for the relatively low strength of the film containing nitrostarch.

I overcome the inherent brittleness of nitrostarch lacquer films by adding a relatively large amount of plasticizer to the lacquer. I have found that in all cases the amount of plasticizer incorporated into the lacquer used for coating flexible sheets must be at least ⅓ of the weight of the nitrostarch present. Unless an "anti-tack" agent is incorporated into the lacquer the amount of plasticizer employed should not exceed ½ of the weight of the nitrostarch present; otherwise the final lacquer film is soft and sticky. Optimum results are obtained when the plasticizer present ranges in amount from 42 to 46% of the weight of the nitrostarch in the lacquer. It will be noted that the proportion of plasticizer employed is greatly in excess of the proportion of plasticizer customarily incorporated into nitrocellulose lacquers in which 5 or 10% of plasticizer by weight of nitrocellulose is ordinarily ample.

Throughout this specification and the appended claims, I use the term "base" to describe those derivatives of carbohydrates, such as nitrocellulose, cellulose acetate, nitrostarch, etc., which are the major film-forming constituents in modern lacquers. By "plasticizers" I mean the class of softening agents such as dibutyl phthallate, etc., which tend to reduce the brittleness of lacquer films and which remain in the film after the solvent employed has evaporated. I employ the term "solvent" to include those organic liquids such as alkyl acetates, ketones, aromatic hydrocarbons, aliphatic hydrocarbons, etc., in which nitrostarch is soluble, and mixtures of these compounds with each other or with diluents such as alcohol. The term "film forming ingredient" is used to include lacquer "bases", plasticizers, resins and the like which have inherent film forming characteristics and remain in the dried lacquer film after the solvent has evaporated. This term does not include pigments, fillers, and like substances which do not themselves have film forming characteristics even though they remain behind after the lacquer solvent has evaporated and comprise a portion of the dried film.

The preferred lacquer of my invention contains only one base, nitrostarch, and in any case, nitrostarch is the principal base and the principal film forming ingredient employed. The addition of other bases, in particular nitrocellulose, tends to cause segregation in the lacquer, even when the viscosity characteristics of the nitrostarch and other base are substantially identical. Upon standing, a lacquer containing nitrostarch and nitrocellulose (both having viscosity characteristics between 4 and 6 centipoises) separates into two layers unless a dispersing agent (such as an alkali soap) is present. This use of a dispersing agent to provide compatibility between the two bases has been suggested heretofore, but I have found that such dispersing agents tend to segregate out of the dried lacquer film, thus spoiling it. Alkali stearates, for example, tend to cause a bloom on the dry lacquer film, thus rendering it unattractive and less resistant to attack.

The nitrostarch which I prefer to employ in the practice of my invention has a nitrogen content ranging from 11.5% to 12.5% and an average viscosity characteristic ranging from 4 to 6 centipoises. Nitrostarch having a nitrogen content below 11.5% by weight tends to produce excessively brittle films. On the other hand, nitrostarch having a nitrogen content in excess of

12.5% is more combustible than nitrostarch of the preferred nitrogen content, and is less readily soluble in most commercial lacquer solvents and solvent mixtures.

By viscosity characteristic, I mean the degree of viscosity which is measured in a standard solvent into which a given proportion of a lacquer base, say nitrostarch, has been dissolved. The figures given for viscosity characteristic have reference to the following well known method:

A solution containing 12% by weight of the lacquer base (say nitrostarch) in a solution consisting of 3 parts butyl acetate and 1 part ethyl alcohol is prepared, and the viscosity of the solution in centipoises at 25° C. is determined, preferably in a viscosimeter of the capillary tube type, or by other standard methods. The resulting determination in centipoises is taken as the average viscosity characteristic of the lacquer base undergoing investigation.

When it is realized that the so-called "low viscosity" nitrocellulose commonly employed in the manufacture of automobile lacquers and the like has an average viscosity characteristic in excess of 150 centipoises as measured in the foregoing method, it will be clear that the nitrostarch which I employ in the practice of my invention has an exceedingly low viscosity characteristic. It is in large part due to this low viscosity characteristic that I am able to put into solution up to 70% by weight of the nitrostarch without increasing the viscosity of the resulting lacquer to a point which precludes its application by customary methods. This proportion of base in lacquer is more than double that of commercial lacquers which have been employed heretofore and enables me to produce exceptionally thick coats on flexible sheets in one application and at the same time permits a tremendous economy in the amount of solvent employed.

My invention will be more thoroughly understood in the light of the following detailed description.

Lacquer is prepared according to any of the suitable conventional methods, but in accordance with one or more of the following rules of formulation:

The lacquer base is preferably nitrostarch alone, and in any case nitrostarch is the principal base.

The nitrostarch base preferably has a nitrogen content ranging from 11.5 to 12.5% and an average viscosity characteristic ranging below 6 centipoises as determined by the method hereinbefore set forth.

In no case should the plasticizer employed be less than 20% by weight of the nitrostarch used.

For paper coating compositions from which the dried films weigh about 5 pounds per 3000 square feet, i. e., with a film thickness below .0003 inch, the ratio of plasticizer to nitrostarch may be kept between 20% and 42% by weight. Such films are very thin, comparable in thickness to those formerly produced on paper by spirit varnishes. If the ratio of plasticizer to nitrostarch in the lacquer is below 20% the film is too brittle and the coated paper tends to curl.

For paper coating compositions from which the dried films weigh about 40 pounds per 3000 square feet, i. e., with a film approximating .002 inch in thickness the ratio of plasticizer to nitrostarch should be between 42 and 46%. Films of this thickness tend to crack upon aging of the coated paper if the ratio of plasticizer to nitrostarch is below about 42%. If the ratio of plasticizer to nitrostarch is above 46%, films of this thickness are very flexible and adherent, but are tacky unless small amounts of one or more "anti-tack" agents such as petroleum jelly, paraffin, stearic acid, or other suitable greasy substance is employed. Usually 2 to 3% by weight of the lacquer of an anti-tack agent is sufficient to overcome tackiness. Films having a thickness approximating .002 of an inch are comparable in thickness to the regenerated cellulose films employed as wrappings.

The best anti-tack agents to employ are greasy hydrocarbons such as petroleum jelly and paraffin. Stearic acid, or other crystalline substances tend to form a bloom if used alone. The tendency of these materials to bloom is inhibited by the presence of hydrocarbons such as paraffin. Thus, when I employ fatty acids and the like, I also incorporate substantially equal amounts of hydrocarbons in the lacquer.

Any suitable plasticizer may be employed, but I prefer to use dibutyl phthalate, triethyl citrate, ethyl phthalyl butyl glycolate, methyl and ethyl ortho benzoyl benzoate, triphenyl phosphate, tricresyl phosphate, triacetin, or mixtures of one or more of these substances. It should be noted that triacetin, triphenyl phosphate and methyl ortho benzoyl benzoate which are unsatisfactory plasticizers for nitrocellulose lacquers, give excellent results in the nitro-starch lacquers of my invention.

Lacquer modifiers and agents for producing special finishes, such as pigments, fillers, metal powders, crystallizing agents, resins, dyes, etc., may be added to the lacquer of my invention in accordance with well recognized conventional methods of formulation.

For producing thick dried films, the lacquer preferably should contain 40% by weight of nitrostarch. With lacquer containing this proportion of nitrostarch, a film of the aforementioned thickness can be produced on paper in a single application. Irrespective of the thickness of film to be produced, it is desirable, of course, to employ as high a ratio of solids (materials which remain in the dry lacquer film) to solvents (vehicles which evaporate) as possible, because this tends to decrease loss of solvent. In general, lacquers of my invention containing 40% and up of nitrostarch, are to be preferred for applying even very thin films to paper.

In accordance with my invention, the dried film which results from a lacquer in which the plasticizer is about 20% of the nitrostarch present will ordinarily be such that the nitrostarch is about 83% of the total film forming ingredients. On the other hand a dried film resulting from a lacquer in which the plasticizer is equal to 50% of the weight of the nitrostarch will ordinarily be such that about 50% of the film forming ingredient is nitrostarch. Accordingly, nitrostarch comprises about 50 to 83% of the film forming ingredients in the dried adherent flexible lacquer films on the flexible sheets of my invention.

The nitrostarch lacquers may be applied to paper and the like in the same manner that varnish, etc., customarily are applied. Reverse roll machines, knife coaters, and various kinds of rolls may be used. Spray coating and brush application also produce satisfactory results, but these methods are relatively slow and expensive.

Any kind of paper, cardboard, rubber and similar flexible materials may be employed in the practice of my invention. Thus adherent, tough,

durable, flexible, brilliant and thick films may be produced on such materials with the nitrostarch lacquers of my invention. I attribute the apparent strength, toughness, flexibility and durability of these lacquer films on flexible backings to the remarkable adhesion developed between the flexible backing and the lacquer film, whereby the film and the backing are enabled to cooperate and the tensile strength of the backing is, in effect, imparted to the whole mass.

The following formulae are intended to be merely illustrative of suitable paper coating compositions made in accordance with my invention. It will be understood that I do not limit myself to the particular plasticizers, solvents, pigments, etc. given in the examples.

Formula 1

	Parts by weight
Nitrostarch, nitrogen content 11.5%–12.5% viscosity characteristic 4–6 centipoises	40
Ester gum	5
Dibutyl phthalate	16
Paraffin	1
Solvent mixture	38
Total	100

Percent solids–62

Formula 2

	Parts by weight
Nitrostarch	50
Triacetin	10
Methyl ortho benzoyl benzoate	10
Ethyl acetate	30
Total	100

Percent solids–70

Formula 3

	Parts by weight
Nitrostarch	39
Ethyl ortho benzoyl benzoate	12
Triethyl citrate	9
Anti-tack agent (paraffin)	1.3
Ethyl acetate	25.0
Soluble	13.7
Total	100

Percent solids–61.3

Formula 4

	Parts by weight
Nitrostarch	52
Triacetin	17
Stearic acid	1
Petroleum jelly	1
Butyl acetate	15
Zylol	14
Total	100

Percent solids–71

By putting both petroleum jelly and stearic acid into this lacquer, tackiness is prevented, and petroleum jelly prevents stearic acid from forming a "bloom" on the dried film.

My invention, in addition to offering a lacquered paper on which the lacquer film is adhesive, flexible, durable and tough, possesses outstanding advantages in that very thick films may be formed at a single application with the expenditure of a small amount of solvent. Moreover, the nitrostarch coating is substantially unaffected by actinic rays, so that it does not discolor appreciably even after long exposure to strong sunlight. In this respect my nitrostarch lacquer is superior to other paper finishes. Consequently where a permanently colorless or transparent film is desired, my invention offers a further advantage. Lastly, the lacquered papers of my invention are substantially free from any tendency to curl, shrink, or wrinkle, and cost less to manufacture because nitrostarch is much cheaper than nitrocellulose having a similar viscosity characteristic. The coatings are thermoplastic, i. e., "heat sealable" and impervious to moisture.

I claim:

1. A flexible sheet having an adherent flexible lacquer film in which the principal base is nitrostarch and containing an amount of plasticizer equal at least to 20% by weight of the nitrostarch in the film.

2. A flexible sheet having an adherent lacquer film in which substantially all of the base is nitrostarch, said film containing a plasticizer in amount equal to at least 20% of the nitrostarch.

3. A flexible sheet having an adherent dry film of lacquer in which at least 95% of the base is nitrostarch, and containing a plasticizer in amount exceeding 20% of the nitrostarch.

4. A flexible sheet having an adherent flexible dry film of lacquer in which the principal base is nitrostarch having an average viscosity characteristic of from 4 to 6 centipoises, and containing a plasticizer in amount exceeding 20% by weight of the nitrostarch.

5. A flexible sheet having an adherent flexible film of lacquer containing at least 50 to 83% by weight of nitrostarch and one or more plasticizers in excess of 20% by weight of the nitrostarch, said plasticizers being selected from the group consisting in dibutyl phthalate, ethyl phthalyl butyl glycolate, methyl ortho benzoyl benzoate, triphenyl phosphate and triacetin.

6. A flexible fibrous sheet having an adherent flexible film of lacquer in which nitrostarch is the principal base and containing from 42 to 46% by weight of the nitrostarch of a plasticizer.

7. A flexible fibrous sheet having an adherent flexible film of lacquer weighing about 5 pounds per 3000 square feet and containing nitrostarch as its principal base, said film also containing a plasticizer in proportions ranging from 20 to 42% by weight of the nitrostarch in the film.

8. A flexible fibrous sheet having an adherent flexible film of lacquer weighing about 40 pounds per 3000 square feet and containing nitrostarch as its principal base, said film also containing an amount of plasticizer exceeding 42% of the weight of the nitrostarch in the film.

9. A flexible fibrous sheet having an adherent flexible film of lacquer weighing about 40 pounds per 3000 square feet and containing nitrostarch as its principal base, said film also containing a plasticizer in amount ranging from 42 to 46% of the weight of the nitrostarch in the film.

10. A flexible fibrous sheet having an adherent flexible film comprising at least one coat of lacquer about .002 of an inch thick in which the principal base is nitrostarch, said coat also containing at least 42% by weight of a plasticizer and a relatively small amount of a greasy substance.

11. A flexible sheet comprising paper having an adherent flexible coating in which the principal base is nitrostarch, the coating also containing plasticizer in excess of 20% of the weight of the nitrostarch.

12. A flexible sheet comprising paper having an adherent flexible coating in which the principal base is nitrostarch having a nitrogen content

ranging from 11.5 to 12.5% as its principal film-forming ingredient, and containing a plasticizer equal in amount to at least 20% of the weight of the nitrostarch.

13. A flexible sheet comprising paper having an adherent flexible coating containing nitrostarch as its principal film-forming ingredient and also containing a plasticizer in amount equal to at least 20% by weight of the nitrostarch in the coating.

14. A flexible sheet comprising paper having an adherent coating containing nitrostarch as its principal film-forming ingredient and containing a plasticizer in amount ranging from ⅕ to ½ the weight of the nitrostarch.

15. A flexible fibrous sheet having an adherent flexible dry lacquer film in which 50 to 83% of the film-forming ingredients is nitrostarch, said film containing an amount of plasticizer not less than ⅕ of the weight of the nitrostarch in the film.

16. A flexible fibrous sheet having adhering thereto a flexible dry lacquer film comprising one or more coats about .0003 of an inch thick in which from 60 to 83% of the film-forming ingredients is nitrostarch having an average viscosity characteristic ranging from 4 to 6 centipoises, said coat containing a plasticizer in amount equal to at least ⅕ of the weight of the nitrostarch present.

17. A flexible fibrous sheet having adhering thereto a flexible dry lacquer film comprising one or more coats about 0.002 of an inch thick in which from 60 to 70% of the film-forming ingredients is nitrostarch having an average viscosity characteristic ranging from 4 to 6 centipoises, said coats containing a plasticizer in amount equal to at least 42% of the weight of the nitrostarch present.

18. A flexible sheet having an adherent flexible lacquer film at least .0003 of an inch thick in which the principal base is nitrostarch, said film containing an amount of plasticizer equal at least to 20% by weight of the nitrostarch in the film.

19. A flexible sheet having an adherent flexible lacquer film of a thickness ranging from .0003 of an inch to .002 of an inch in which nitrostarch is the principal base, said film containing an amount of plasticizer ranging from 20% to 46% by weight of the nitrostarch in the film.

20. A flexible sheet having an adherent flexible lacquer film at least .002 of an inch thick in which the principal base is nitrostarch, said film containing an amount of plasticizer which is at least 42% by weight of the nitrostarch in the film.

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