

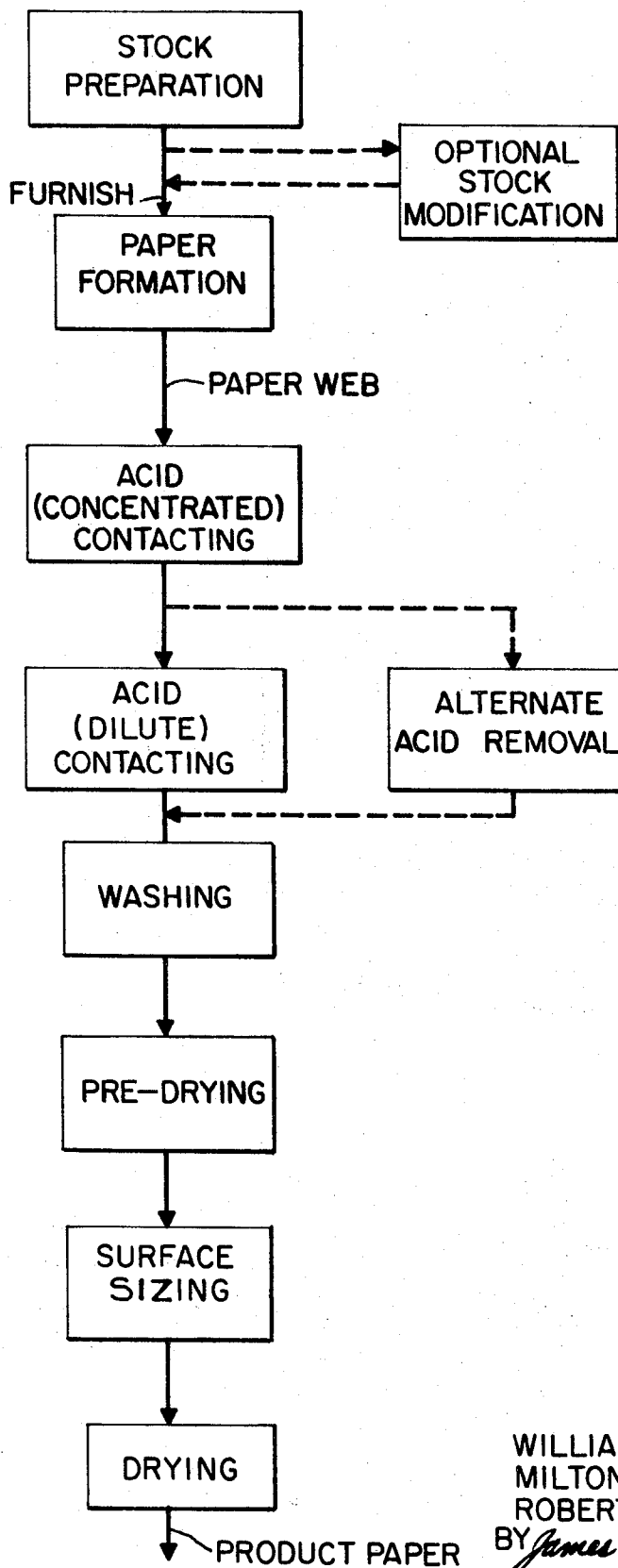
Feb. 9, 1971

W. R. WASKO ET AL

3,562,099

ERASABLE PAPER AND PROCESS FOR MAKING SAME

Filed Jan. 17, 1968



INVENTORS.

WILLIAM R. WASKO
MILTON R. SHEPPARD
ROBERT J. EBER

BY *James Albert Krohila*
ATTORNEY.

1

3,562,099

ERASABLE PAPER AND PROCESS FOR MAKING SAME

William R. Wasko, 201 Cleveland Ave., Cherry Hill,
N.J. 08034; and Milton R. Sheppard, 27 Bermuda Circle,
and Robert J. Eber, 21 Mullshire Lane, both of
Willingboro, N.J. 08046

Filed Jan. 17, 1968, Ser. No. 698,473

Int. Cl. D21h 3/08, 3/20, 3/28

U.S. Cl. 162—135

8 Claims

ABSTRACT OF THE DISCLOSURE

Process for making erasable paper by forming a paper web, contacting the formed web with a parachmentized solution, removing excess acid, at least partially drying the web, and applying to a surface of the paper one or more sizing agents which are fluorinated carboxylic acids, and are preferably perfluorinated carboxylic acids, and are applied alone or in combination with certain additives. The invention also includes the product of the foregoing process.

BACKGROUND OF THE INVENTION

(a) Field of the invention

The instant invention relates to cellulosic sheet materials such as paper. More particularly, it is directed to a novel writing paper having superior erasability characteristics, and to the process for making such paper.

(b) Description of the prior art

Heretofore, attempts have been made to produce a writing paper from which typewriting could be erased easily and practically completely by means of a soft rubber eraser rather than an eraser of the hard abrasive type such as is commonly required for the erasure of typewriting. These past attempts have involved the application of a thin coating of suitable size, such as casein or gum arabic, to the surface on both sides of the paper sheet. It has been suggested that this prior coating technique depends for its effectiveness upon the presence of a superimposed, uniform, thin coating of size on the surfaces of the paper, whereby the paper is protected from ready access by constituents of the ink which otherwise would penetrate the paper and render the writing indelible.

In accordance with past practice, a somewhat readily erasable writing paper has been produced by dipping the paper in a solution of a suitable size coating, followed by removal of the excess coating. This operation is repeated several times in order to build up a sufficiently heavy layer of coating to give the desired degree of erasability. More recently, the coating technique has been modified so as to constitute one continuous operation involving a series of brief dippings. Great care must be taken in practicing the coating method to ensure application to the paper of the proper amount of size, since too little size coating does not give the desired degree of erasability and too much will cause the ink to smear excessively. The thickness of the size coating ultimately built up upon the surfaces of the paper is controlled, to some degree, by regulating the viscosity of the coating solution within defined limits.

Readily-erasable papers heretofore made, suffer from a number of distinct and significant disadvantages. First of all, with the prior technique it is very difficult, if not impossible, to ensure a uniform erasability characteristic from one surface of the paper sheet to the other, and from end to end on a roll of paper. This failing arises from the impossibility of providing an absolutely uniform thick-

2

ness of size on all surfaces of the paper. A further failing of prior readily-erasable papers is their "tacky" feel and their susceptibility to moisture. In addition, it has been found that the coating sizes commonly employed in prior techniques have a tendency to discolor and become somewhat brittle on aging, causing the coated paper also to become more yellow and brittle with age than normally would be expected. Still another disadvantage is the tendency of present day size coatings to cause the coated paper to become more transparent, which also is undesirable in most writing papers.

In view of the above, it is a principal object of the instant invention to provide a novel and improved writing paper, including particularly an improved paper for typewriting, and a novel method of preparing and treating paper to achieve this result. A further and more specific object is to provide a novel writing paper exhibiting superior erasability characteristics with respect to typewriting, and resistance to feathering by typing inks. Still another and major object is to provide a new and improved paper, including particularly a typewriting paper, and a novel process for making same, which preferentially in the practice of the invention involves modification of the base paper stock or "furnish," as well as treatment of the paper formed therefrom, in order to achieve superior whiteness and opacity in addition to superior erasability in the product paper. These and other objects and advantages of the instant invention will become more readily apparent from the following detailed description of the invention, which is to be read in the light of the accompanying drawing.

SUMMARY OF THE INVENTION

It has been found that, by subjecting paper to contact for a defined period of time with a relatively concentrated aqueous sulfuric acid solution of defined strength, the paper is rendered more readily erasable, particularly with respect to typewriting. It also has been found that paper base stocks, or "furnishes," which have been modified in a novel way by the addition of certain additives provide superior and therefore preferred base stocks for making more readily erasable paper in accordance with the present invention. Specifically, it has been found that practice of the latter, preferred embodiment of the instant invention results in the production of product papers which exhibit superior whiteness and opacity, as well as superior erasability, rendering them particularly suitable for commercial sale and use as a writing paper and particularly as a typewriter paper. Furthermore, it also has been found that through the application of a small amount of one or more selected sizing agents to the surfaces of the paper after acid contact and removal, and after at least partial drying, the tendency of typing inks to "feather" or "wick" on the product paper is markedly reduced over that observed with such paper which is not so coated. Accordingly, the latter technique constitutes an essential element of the present invention.

DESCRIPTION OF THE DRAWING

The accompanying drawing illustrates schematically the practice of the instant invention in its several embodiments, and the positioning thereof in the sequence of conventional paper-making operations. Thus, practice of the preferred technique herein disclosed, of modifying the paper base stock through the addition thereto of one or more of certain additives, takes place during the steps constituting the conventional stock preparation and prior to the conventional paper formation step. Following formation, the web of paper is contacted with the relatively concentrated aqueous solution of sulfuric acid, and the

acid subsequently removed by one of several alternate techniques such as by contacting with a relatively dilute aqueous solution of sulfuric acid, by neutralization of the residual acid, or the like. Following the removal of the residual acid, the paper web is washed and at least partially dried preliminary to the surface application, as herein disclosed, of one or more selected sizing agents by conventional techniques and apparatus. Following such surfaces application, the drying is completed, if necessary, to produce the finished product paper.

DETAILED DESCRIPTION OF THE INVENTION

In practicing the instant invention, paper is contacted for a defined period of time with a contacting agent consisting essentially of a concentrated aqueous solution of sulfuric acid of specified strength. Normally, aqueous sulfuric acid solutions containing from about 60 to about 77 percent by weight of sulfuric acid provide satisfactory results and can be used. However, sulfuric acid concentrations in the range of from about 65 to about 72 percent by weight give superior results and therefore are preferred for use. Under certain circumstances, however, the aqueous sulfuric acid solution having concentrations of sulfuric acid either above or below the above-recited ranges also may provide satisfactory results.

It is critical to the achievement of satisfactory results in the practice of the instant invention that the paper remain in contact with a concentrated aqueous sulfuric acid solution of suitable strength for a sufficient but limited period of time. Thus, the total contact time between the paper and the specified acid solution should be somewhere in the range of from about 1 to about 20 seconds. Contact times somewhat in excess of 1 second, for example between 4 and 12 seconds, provide superior results and are preferred, although the contact time normally should not exceed 20 seconds. Generally, the contact time required to give satisfactory results will vary, within the recited range, inversely as the strength of the concentrated aqueous sulfuric acid solution is varied within its above-specified range. Thus, concentrations of acid in the lower portion of the range indicated to be suitable will require contact times in the upper portion of the suitable range of times, and vice versa. For acid concentrations in the preferred range of from about 65 to about 72 percent by weight of sulfuric acid, contact times of from about 5 to about 10 seconds have been found to provide excellent results.

The temperatures at which the contacting of the paper with the relatively concentrated acid solution takes place is not particularly critical. Generally, however, an increase in contact temperature has been found to be helpful in producing satisfactory results where it is desired to compensate for a decrease in suitable acid strength, or suitable contact time, or both. Contact temperatures in the range of from about 50° F. to about 70° F. produce satisfactory results and can be employed, although contact temperatures in the range of from about 55° F. to about 65° F. are preferred. On occasion, contact temperatures outside of the aforementioned ranges can be employed.

Contacting between the concentrated aqueous solution of sulfuric acid and the paper can be effected by suitable conventional techniques and apparatus. Normally, the contacting will be accomplished by immersing or dipping the paper in a liquid phase or bath consisting essentially of the concentrated aqueous solution of sulfuric acid and leaving the paper in contact with the acid, either immersed or simply wet with the acid, for the required contact time and under the recommended contact temperatures. This contacting may be batch-wise, although continuous operation is preferred, involving continuously passing the paper through the acid bath, which is either contained or flowing concurrently or countercurrently with the web of paper.

After the paper has been sufficiently contacted with the concentrated aqueous solution of sulfuric acid, it can be subjected to conventional techniques and apparatus to remove substantially all of the remaining acid solution.

Such techniques include, for example: thoroughly washing the contacted paper with water; neutralizing the residual acid with a suitable alkaline material, followed by washing with water; and the like. Another, and preferred, alternative is to contact the paper containing the residual, relatively concentrated aqueous sulfuric acid solution first with a relatively dilute aqueous solution of sulfuric acid, and finally with water in order to remove substantially all remaining traces of acid. This alternative is carried out conveniently by a succession of contacts, in over-all countercurrent relationship, between the paper containing the residual, relatively concentrated aqueous sulfuric acid solution and a stream of water which becomes progressively richer in sulfuric acid with each successive contact with the paper. In any event, the paper ultimately is dried by conventional methods and apparatus. After at least partial drying is effected, however, it is necessary to make the before-mentioned surface application of the selected sizing agent or agents.

Paper which has been treated with relatively concentrated aqueous sulfuric acid solution in accordance with the present invention exhibits erasability characteristics, particularly with respect to typewriting, which are superior to those possessed by paper rendered more readily erasable by techniques heretofore known in the art. Thus, by the acid contacting technique of the present invention it is possible, and indeed normal, to produce a product paper exhibiting an erasability which is absolutely uniform from one surface of the paper to the other, and from end to end on a large roll of paper. This is in decided contrast to papers rendered more readily erasable by conventional coating techniques, where the thickness and evenness of the coating, and consequently the uniformity of the erasability, very often varies from surface to surface and from end to end on the paper. In addition, paper treated with sulfuric acid in accordance with the present invention does not exhibit the same tendency to discolor and becomes brittle with age as do conventionally-coated papers, and does not show the same susceptibility to moisture and tendency to feel "tacky" to the touch as the conventional coated papers. Furthermore, by the instant technique of applying a selected sizing agent or agents to the surface of the acid-treated paper, the tendency of typewriting to "feather" or "wick" on such paper is markedly reduced.

While the erasability characteristics of any paper can be substantially improved by subjecting it to treatment in accordance with the instant invention, it also has been found that when conventional paper stocks are modified as hereinafter described, a base paper stock or furnish is produced which exhibits superior qualities with respect to its use in forming paper to be further processed in accordance with the present invention. This method of paper stock modification followed by acid treatment and surface sizing constitutes a preferred embodiment of the instant invention, in that it produces a product paper exhibiting among other things superior opacity and whiteness for commercial use and sale as a typewriter paper.

In general, it has been found that by incorporating small but sufficient amounts of one or more of certain additives into conventional paper stocks comprising for example either wood or rag pulps, a paper can be conventionally formed which, upon acid treatment in accordance with the present invention, also exhibits a superior whiteness and opacity in addition to more ready erasability. Paper stock modification in accordance with the instant invention is particularly beneficial with respect to parchmentized papers. This is for the reason that paper stocks of the absorbent-paper type, such as are commonly employed in manufacturing parchmentized papers, typically produce a paper of commercially-undesirable translucency after acid treatment to improve erasability.

In accordance with the preferred embodiment of the present invention, an improved paper stock is prepared by incorporating one, some or preferably all of the follow-

ing additive materials in a stock comprising rag or wood pulp: (1) a small amount, sufficient to reduce significantly paper transparency, of an opacifying filler or pigment; (2) a small amount, sufficient to reduce significantly paper absorbency, of a sizing agent; (3) a small amount, sufficient to improve significantly paper wet strength, of a wet strength improving agent; and (4) a small amount, sufficient to improve optical brightness, of an optical brightening agent.

Opacifying filler or pigments which are suitable for use in accordance with the invention are those which do not react with acids and which, in small but sufficient amounts, impart the desired degree of opacity to the product paper. Suitable fillers include naturally-occurring inorganic substances, such as talc, silica, certain clays and the like, or synthetic substances such as barium sulfate, titanium dioxide pigments and the like. The use of an opacifying agent is optional but is preferred in the practice of the instant invention, and the use of titanium dioxide as a filler is distinctly preferred. Generally, the opacifying filler, for example titanium dioxide, is incorporated in the paper stock in a small but sufficient amount, generally equivalent to from about 2 to about 8 percent by weight of the pulp on a dry basis. Amounts of the opacifying filler approximate 5 percent by weight of the dry pulp give excellent results and are preferred. It also is contemplated as within the scope of the instant invention to incorporate in the paper stock pigments or fillers other than white in color, in order to produce product papers having a desired color.

Sizing agents, or sizes as they often are called, which are suitable for use in modifying the paper stock in accordance with instant invention are those which, in small but sufficient amounts, are capable of suitably reducing the permeability of the formed paper to subsequent penetration by the liquids, and in particular by the concentrated aqueous solution of sulfuric acid. Suitable sizing agents, or sizes, are generally well known, and include substances such as rosin sizes, animal glues, starches, gelatin, wax emulsions, fatty acid-amine condensates and the like. Aqueous emulsion polymers which do not undesirably color the stock also are suitable, such as aqueous emulsions of: acrylic polymers (for example, "Goodrich 2600 X84"); Buna rubber (for example, "Hycar 1552"); butadiene polymers and copolymers (for example, "Dow 636"); rubber latex; and the like. In the practice of the present invention, the use of a size or sizing agent, and particularly of a rosin size, is distinctly preferred.

The exact amount of the sizing agent required to be added to the paper stock or furnish in order to impart a sufficient reduction in paper absorbency can be determined readily by experiment. Generally, however, amounts of the sizing agent, for example, rosin size, equivalent to from about 1/4 to about 3 percent by weight of the pulp on a dry basis are suitable, although amounts equivalent to approximately 2 percent by weight of dry pulp give excellent results and are preferred. If desired, the necessary amount of size also can be reduced by an increase in the severity of the stock preparation conditions, for example, by an increase in beating, to produce a more dense and, consequently, less porous paper.

The wet strength agent to be added to the paper stock in practicing the instant invention can be any such known agent which, in small but sufficient amount, is suitable for imparting the desired improvement in wet strength necessary to sustain the paper during subsequent acid treatment in accordance with the instant invention. Wet strength agents are well known in the art. See, for example, U.S. Pat. Nos. 3,129,133; 3,146,158; and 3,151,017 for many specific examples of suitable wet strength agents. Melamine formaldehyde resins and urea formaldehyde resins which are water-dispersible and of suitable quality have been found to be particularly useful. Generally, the amount of the wet strength agent required to be incorporated in the paper stock to impart

the desired degree of improvement in paper wet strength can be determined readily by experiment. However, the usual wet strength agents normally are incorporated in paper stock in amounts equivalent to from about 1/4 to about 3 percent by weight of the paper pulp on a dry basis, and suitable melamine formaldehyde resin and urea formaldehyde resin wet strength agents are satisfactorily employed in amounts approximating 2 percent. The use of a wet strength agent in the practice of the invention is distinctly preferred.

Optical brightening agents which are suitable for use in modifying the paper stock in accordance with the instant invention are those which, in small but sufficient amounts, are capable of improving the optical brightness and color uniformity of the product paper to the desired degree. Suitable optical brightening agents are generally well known and include substances such as the sodium salt of triazinyl diamino stilbene disulfonic acid. The use of an optical brightening agent in the practice of the present invention is optional but is preferred, and the use of the sodium salt of triazinyl diamino stilbene disulfonic acid is distinctly preferred. Such an optical brightening agent is available commercially from Sandoz, Ltd., of Basle, Switzerland, under the brand name, "Leucophor BS." The exact amount of the optical brightening agent required to be added to the paper stock in order to impart the desired improvement in optical brightness and color uniformity can be determined readily by experiment. Generally, however, amounts of the selected optical brightening agent, such as for example, the sodium salt of triazinyl diamino stilbene disulfonic acid, equivalent to from 0.03125 to about 0.125 percent by weight of the pulp on a dry basis are suitable, although amounts equivalent to approximately 0.0625 percent by weight on the same basis give excellent results and are preferred.

In practicing the instant invention, the above-mentioned additive materials are incorporated in the stock preparation stage, i.e., during the conventional beating or refining operations, or in both. In this manner the additives are uniformly distributed throughout the stock, and ultimately throughout the paper after the latter is formed by conventional techniques and machines.

Conventional paper stocks comprising rag or either hard or soft wood pulps can be used in the practice of the present invention. For example, suitable pulps include bleached and semi-bleached sulfate and sulfite fiber pulps and blends thereof with each other and the like. Pulp fibers known and available commercially under such brand names as "Vigorwhite," "Cedaniel," "Brunswick," all of which are 100% softwood bleached sulfate pulps, and "Espanola" which is a 50/50 blend of bleached hardwood and bleached softwood, produced by a sulfate process can conveniently be used.

As noted above, the acid contacting in accordance with the present invention of a paper made from either a nonmodified or modified paper stock produces a marked improvement in the erasability of such paper, particularly with respect to typewriting. The modification of the paper stock as herein disclosed provides an additional benefit in that the product paper exhibits superior opacity, superior whiteness or brightness, and greater wet strength, all of which makes such paper more attractive from a commercial standpoint. However, it also has been observed that a paper rendered more readily erasable by practice of only the acid-contacting technique of the present invention exhibits an undesirable susceptibility to smudging by the usual typing inks, and to "wicking" or "feathering" by such inks, including after erasure and retyping. Accordingly, while the erasability characteristics of the acid-treated paper were superior and indeed outstanding, the significant tendency of such paper to promote smudging and wicking or feathering of typing inks left something to be desired.

As heretofore noted, it also has been found that at least the tendency of the acid-treated paper to promote

ink wicking or feathering can be substantially eliminated or significantly reduced by the technique of applying one or more selected sizing agents to the surface of the acid-contacted paper following acid removal and washing, and after at least partial drying of the paper.

The sizing agents herein disclosed as suitable are the fluorinated carboxylic acids, including the perfluorinated carboxylic acids, used either alone or in combination with a suitable starch or a suitable water-soluble gum. Suitable starches include unmodified starches and modified starches such as chlorinated starches, ethylated starches, acetylated starches and the like. Suitable water-soluble gums include such substances as carboxymethylcellulose, methylcellulose, ethylcellulose, polyvinyl alcohol, latex emulsions, animal glues, proteins such as casein and soya protein, and the like. Suitable agents of all of these types are well known, and many are commercially available. For example, the product sold commercially by the Minnesota Mining & Manufacturing Company of Saint Paul, Minn., under the brand name, "FC 806," has been found to be particularly satisfactory and is preferred for use. This product consists essentially of a fluorocarbon material of the type herein disclosed as suitable for use as a sizing agent.

The surface application of the sizing agent can be effected conveniently by conventional techniques and conventional equipment such as sizing equipment. Generally, the sizing agent is applied in the form of a solution, typically aqueous. In the case of "FC 806," for example, such solution consists of from about 0.1 to about 0.5 percent by weight of the active agent of "FC 806" in water, although a concentration of approximately 0.25 percent has been found to be particularly satisfactory and is preferred. The aforesaid aqueous solution of the sizing agent is applied to the at least partially-dried web of acid-contacted paper through the nip of a conventional size press applicator, and in an amount sufficient to result in the addition on a water-free basis of from about 0.01 to about 0.05 pound of the fluorocarbon sizing agent for each 3,000 square feet of paper (i.e., 500 sheets, each 24" x 36"). In the case of "FC 806," the addition of approximately 0.025 pound of the active sizing agent in that product on a water-free basis per 3,000 square feet has been found to give excellent results.

Although a fluorocarbon sizing agent such as "FC 806" produces excellent results when employed alone, it also may be used together with other materials such as suitable starches or water-soluble gums. When such an additional material is used, it also is applied in the aqueous solution and therein at a concentration of from about 2 to about 10 percent by weight, with 6 percent being typical. At such concentrations, the additional material is applied to the paper web at a rate equivalent, on a dry basis, to from about 0.2 to about 1.0, and typically 0.5, pound of the additional material per 3,000 square feet of paper stock. Higher applications, viz., up to 2 pounds per 3,000 square feet, on occasion have been found desirable, and these require a correspondingly higher solution concentration.

Reference is again made to the accompanying figure for a schematic illustration of the sequence of operations in practicing the instant invention in its several embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to illustrate a specific and preferred embodiment of the invention, a paper base stock or furnish is prepared in a conventional manner comprising 100 weight percent of a bleached hardwood pulp available commercially under the brand name, "Espanola." This pulp is suitable for manufacturing an absorbent type paper (commonly referred to as "water leaf"), which typically is used in the manufacture of parchment paper. In accordance with the preferred practice of the invention, this

furnish is modified so as to produce a superior base stock for making a more readily erasable paper as herein disclosed. Specifically, there is incorporated in such furnish approximately 5 percent of a titanium dioxide opacifying filler available commercially under the brand name, "Rayox," approximately 0.25 percent of a rosin size available commercially under the brand name, "Cyfor," approximately 0.25 percent of a melamine formaldehyde resin wet strength agent available commercially under the brand name, "Parez 607," and approximately 0.0625 percent of an optical brightening agent available commercially under the brand name, "Leucophor BS." The aforesaid percentages are by weight, and are based on dry pulp. After suitable preparation steps, such as beating, refining or both, the modified furnish so prepared is formed into an absorbent paper sheet material by conventional machines and techniques of the Fourdrinier type.

The paper sheet material formed as above described is continuously contacted with a relatively concentrated aqueous solution of sulfuric acid, containing approximately 68 percent by weight of sulfuric acid, and is allowed to remain in contact therewith for a total contact time of approximately 5 seconds. This contact is effected by continuously running the paper sheet material or web, submerged, through a liquid phase or bath consisting essentially of the above-specified, relatively concentrated aqueous sulfuric acid solution, and, after emergence, allowing the paper to remain substantially wet with the acid solution for the balance of the specified 5-second contact time. The temperature of the bath, i.e., the contact temperature, is maintained relatively constant at about 60° F.

After emergence from the relatively concentrated aqueous sulfuric acid solution, the paper is continuously contacted with a relatively and substantially more dilute aqueous solution of sulfuric acid, typically containing approximately 35 percent or less by weight of sulfuric acid. As before, contacting conveniently can be effected by continuously passing the paper sheet material, submerged, through a liquid bath consisting essentially of the relatively dilute aqueous sulfuric acid. However, this contacting preferably is effected countercurrently, by passing the paper continuously through a countercurrent liquid stream which consists initially of water. In this case of contacting with dilute acid solution, the contacting need only be sufficiently long to accomplish an adequate mixing of the two acid solutions. The contact temperature is maintained in the range of from about 50° F. to about 100° F.

After the paper sheet material emerges from the relatively dilute aqueous sulfuric acid solution, it is thoroughly washed, if necessary with an excess of water, until substantially all of the acid is removed. Prior to a final water wash the paper web is contacted with an aqueous ammonium hydroxide solution to remove remaining traces of acid and adjust the pH of the paper to approximately 8.0 to 8.5. The resulting paper sheet material, substantially free of residual acid, then is subjected to drying by means of conventional equipment and techniques.

After at least partial drying, the surface application of a sizing agent is effected in the nip of a conventional size press applicator, through which the at least partially dried web of acid-treated paper is progressing. The sizing agent employed in this embodiment is the fluorocarbon product available commercially from the Minnesota Mining & Manufacturing Company under the brand name, "FC 806." The material for application consists essentially of an aqueous solution containing approximately 0.25 percent by weight of the active sizing agent of "FC 806" in water. This aqueous solution of sizing agent is applied at the rate, on a dry basis, of approximately 0.025 pound of solute fluorocarbon per 3,000 square feet of paper. After application of the sizing agent, the web is further dried by means of conventional equipment and techniques.

The paper prepared as above described then is sub-

jected to comparative testing: (a) with paper prepared identically and from the same paper stock which paper has been acid contacted but has not been given a surface application of the sizing agent; and (b) with a conventional and standard 25 percent rag pulp Bond paper available commercially and illustrative of a typical high quality typewriter paper. To each of such specimens identical typewriting then is applied in an identical manner and utilizing a single-use, carbon ribbon. Each specimen then is examined or tested in substantially identical manner for, among other things, erasability and resistance to ink feathering or wicking. The results of all such tests are evaluated and compared visually and in the same manner. The following tabulation illustrates the results which are achieved:

Paper stock	Erasability	Resistance to feathering
Conventional (untreated) bond paper.....	Poor.....	Excellent.
Acid-treated paper.....	Good.....	Poor.
Acid-treated and surface-sized paper.....	Excellent....	Excellent.

As will be seen from the foregoing results, the product paper produced by practice of the acid-contacting technique of the invention exhibits in both instances an erasability which is superior to that possessed by the conventional Bond typewriter paper which is not so treated. However, it also will be noted that the paper stock which is subjected only to the acid contacting step is inferior to the untreated conventional Bond paper with respect to its resistance to ink feathering. Nevertheless, the paper stock which is subjected to the practice of the present invention in its preferred form, i.e., a combination of acid treatment and surface sizing, exhibits excellent resistance to ink feathering in addition to superior erasability. The observed excellence in resistance to ink feathering is particularly desirable, and unexpected, in view of the somewhat poorer results in this regard achieved with other sizing agents tested. Results substantially similar in all respects are achieved when the same tests are conducted utilizing a cloth, multi-use, typewriter ribbon instead of a carbon ribbon.

It also should be noted that each of the papers described above, being made from a furnish which had been modified with additives in accordance with the present invention, exhibits an opacity and whiteness rendering it of relatively superior quality for commercial sale and use as a typewriter paper.

When the above-described acid treatment and surface sizing operations are carried out in connection with papers produced without modification of the furnish through the addition of additives, there is produced a product paper exhibiting substantially the same superior erasability characteristics and the same improved resistance to ink feathering as the paper resulting from the practice of the instant invention in its entirety. However, the paper produced without the stock modification steps of the instant invention generally is not as desirable commercially because of its relatively poorer opacity and whiteness.

The invention claimed is:

1. Process for making an improved erasable paper which comprises:

- (a) forming a paper sheet from a cellulosic pulp;
- (b) contacting said paper sheet with an aqueous solution of sulfuric acid containing from about 60 to about 77 percent by weight of sulfuric acid for a

total contact time in the range of from 1 to about 20 seconds;

(c) removing substantially all of said acid from the contacted paper;

(d) at least partially drying said sheet; and

(e) applying to the surface of said paper sheet a sizing amount of a sizing agent selected from the group consisting of (1) at least one fluorinated carboxylic acid, (2) a mixture of (1) with a starch, and (3) a mixture of (1) with a water-soluble gum.

2. Process according to claim 1, including the steps of adding to said pulp a brightening amount of an optical brightener and an opacifying amount of an opacifying filler.

3. Process according to claim 1 wherein said sizing agent is at least one perfluorinated carboxylic acid.

4. Process according to claim 1 wherein said sizing agent is at least one fluorinated carboxylic acid and is applied in an amount of from about 0.01 to about 0.05 pound per 3,000 square feet of dry paper sheet.

5. As an article of manufacture, improved erasable paper produced by a process which comprises:

(a) forming a paper sheet from a cellulosic pulp;

(b) contacting said paper sheet with an aqueous solution of sulfuric acid containing from about 60 to about 77 percent by weight of sulfuric acid for a total contact time in the range of from about 1 to about 20 seconds;

(c) removing substantially all of said acid from the contacted paper;

(d) at least partially drying said sheet; and

(e) applying to the surface of said paper sheet a sizing amount of a sizing agent selected from the group consisting of (1) at least one fluorinated carboxylic acid, (2) a mixture of (1) with a starch, and (3) a mixture of (1) with a water-soluble gum.

6. An article according to claim 5 wherein said paper sheet includes up to about 0.125% by weight of the pulp on a dry basis of an optical brightening agent and up to about 8% by weight of the pulp on a dry basis of an opacifying filler.

7. An article according to claim 5 wherein said sizing agent is at least one perfluorinated fluorinated carboxylic acid.

8. An article according to claim 5 wherein said sizing agent is at least one fluorinated carboxylic acid and is applied in an amount of from about 0.01 to about 0.05 pound per 3,000 square feet of dry paper sheet.

References Cited

UNITED STATES PATENTS

2,156,755	5/1939	Fuelnegg	117—153
3,184,373	5/1965	Arledter	162—178X
2,459,743	8/1969	Zussman	162—162X
3,471,362	10/1969	Kent	162—178

OTHER REFERENCES

Casey "Pulp & Paper," vol. II, 2nd edition, 1960, Interscience Publishers, Inc., N.Y., p. 654.

S. LEON BASHORE, Primary Examiner

F. FREI, Assistant Examiner

U.S. Cl. X.R.

8—119; 117—153; 162—158, 162, 175, 178, 181