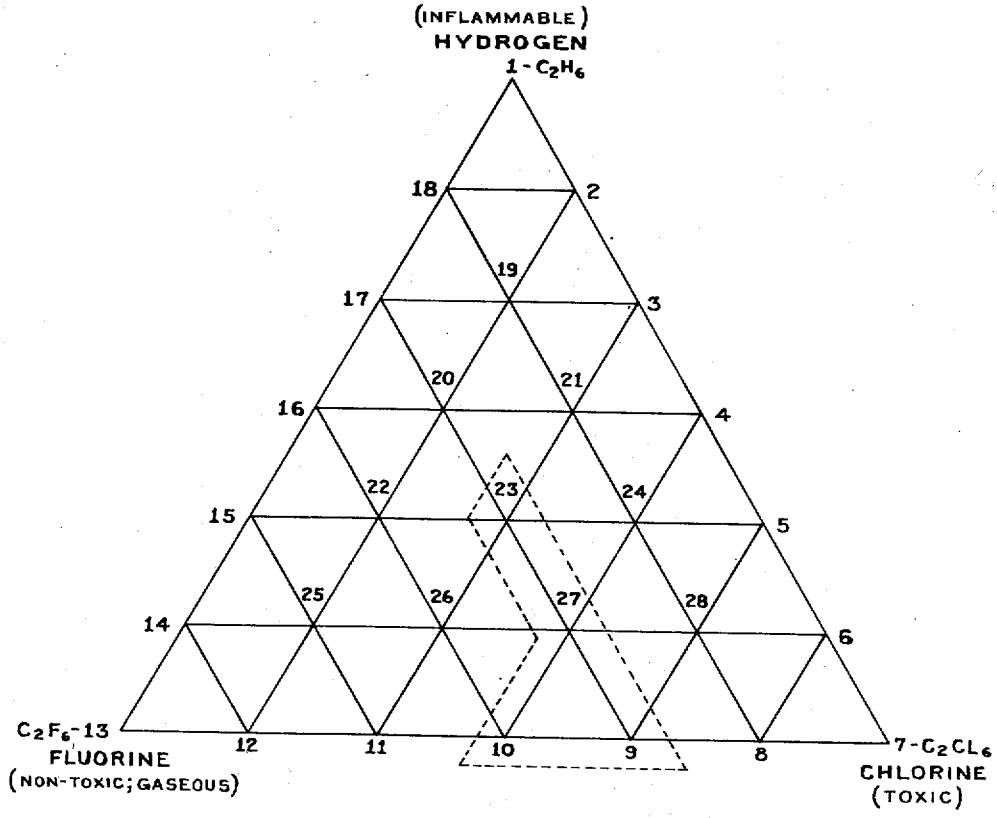
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PRINTING INK

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PRINTING INK

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This invention relates to rotogravure inks, and more particularly to rotogravure inks which are both non-toxic and non-inflammable.

The rotogravure printing process as usually carried out involves printing from an intaglio roll with relatively fluid inks which dry by the evaporation of very volatile solvents. Such solvents have been selected in the past so as to dissolve the binder used, and to provide evaporation at the desired very rapid rate. Unfortunately, all such solvents have been either highly toxic or inflammable, and the majority have possessed both of these undesirable characteristics. This is particularly true of the aromatic hydrocarbons such as benzol and toluol which heretofore have been considered the rotogravure solvents of greatest utility.

The very nature of the printing press operation makes control of the resulting fire and health hazards extremely difficult if not impossible. No simple ventilation system has been devised which will remove the vapors from the region of the presses to such an extent as to eliminate localized high concentration of the solvents in positions in which the workmen will be exposed to their toxicity. The character of the presses used makes a satisfactory solvent recovery system such as used in some other industries difficult and expensive because of difficulties of applying such a system to a machine handling a printed web or sheet which will not contact or smudge the freshly printed subject. The rapid operation of the machines causes continuous generation of static electricity, and although this is systematically eliminated ordinarily by grounded conductors, sparks are by no means infrequent and if such a spark occurs in the presence of an explosive or inflammable solvent mixture, a dangerous fire is likely to result, the seriousness of which is further increased by the presence of large quantities of paper upon the presses and at other points in the pressrooms.

Ever since the development of rotogravure printing a constant but unsuccessful search has been carried on to find or devise practicably usable solvents or solvent combinations suitably free of the hazards of toxicity and inflammability. As a result solvents have been found which were free of one or the other of the two hazards, but in no case were both hazards eliminated in any usable solvent or solvent combination.

Recently, the extreme toxicity of the usual aromatic hydrocarbon materials has caused the substitution, in certain cases, of other materials found to be functionally sufficient and also less toxic—for example, the petroleum hydrocarbons in admixture with certain other organic solvents. These substitution solvents decreased the health hazard, but failed to eliminate the fire hazard, as the petroleum hydrocarbons found usable are even more inflammable than the aromatic solvents of the same volatility. Of course, non-inflammable solvents are known—e. g., the chlorinated hydrocarbons, such as carbon tetrachloride; but such solvents are too toxic for printing inks, being as injurious or even more so than the aromatic hydrocarbons.

It is an object of the present invention to provide adequately and commercially available rotogravure printing inks which are non-toxic and non-inflammable in use.

It is another object to provide a solvent for the binder of an ink which is sufficiently volatile for rotogravure inks, and the like, and which still gives fumes on evaporation which are free from the objectionable health hazards of undue toxicity and inflammability.

It is still another object to provide certain fluorochloroalkanes having a predetermined composition selected to give an intermolecular relationship which gives an evaporation range within the temperature limits of substantially 40° to 200° C.; adequate solvent powers for the resins, bitumens, cellulose acetates, etc., ordinarily used as the binder of rotogravure inks, or the like; and which also are substantially free from objectionable toxicity and inflammability, in use.

It is a further object of the invention to provide such a non-toxic and non-inflammable solvent consisting of a fluorochloroalkane in which the substitution of the fluorine and chlorine is controlled to give a predetermined limited relationship of fluorine to chlorine, and the fluorine and chlorine jointly are controlled with reference to the retained hydrogen to give a predetermined relationship in which the summation of the fluorine plus chlorine is at least one-half the retained hydrogen.

Further objects and advantages of the invention will appear as hereinafter set forth.

In the practical use of my invention fluorochloroalkanes are utilized as a part or all of the solvent component of my rotogravure ink. It has long been known that the chlorinated hydrocarbons are all highly toxic; and more recently it has been discovered in connection with certain chlorinated compounds, that if part of the chlorine of such chlorinated hydrocarbons is replaced by fluorine—another highly toxic material—the resulting compound retains its non-inflammability characteristics and also is relieved of its toxicity.

I have now discovered that certain fluorochloro substituted hydrocarbons of predetermined intermolecular relationship can be used to prepare rotogravure inks which are completely non-inflammable in use, and which are likewise com-

pletely innocuous as to toxicity. These certain fluorochloroalkanes have been discovered to be adequate solvents to put in solution a sufficient amount of gum, resin, etc., to give a binder of such viscosity, metal adhesion, solvent release, etc., as to serve as a practicably sufficient solvent for rotogravure inks and the like and to provide inks of the desired non-toxic and non-inflammable characteristics. These fluorochloroalkanes are suitable solvents for the gums, resins, and bitumens, and also for the cellulose derivatives and the like, used in the manufacture of rotogravure inks, and can be used either alone or when properly admixed with other solvents.

Also, I have now found that certain fluorochloroalkanes have suitable solvent characteristics and also, when in solution, have such volatility as to give evaporation and solvent release equal to high grade rotogravure inks such as those now made and used commercially. In selecting rotogravure solvent combinations made up of fluorochloroalkanes of the proper relationship to give the desired non-toxic and non-inflammability characteristics, I have found that nevertheless a wide range of boiling points and volatilities are available, so that suitable inks of any desired "speed" or evaporation rate may be secured. And for inks comparable in evaporation speeds to those presently used in industry, fluorochloroalkanes of similar or somewhat higher boiling points can be used. The fluorochloroalkanes used in general have volatilities somewhat higher than hydrocarbons of corresponding boiling points, so that a higher boiling fluorochloroalkane can be used to obtain an ink of the same speed of evaporation.

According to present chemical knowledge available to me, all the theoretically possible fluorochloroalkanes derivable from a given hydrocarbon can be mathematically determined. The accompanying chart, which is set forth for illustrative purposes in describing my invention, shows all the possible fluorochloro substitutions of ethane. That is, all the various combinations of 2 carbon atoms with hydrogen, chlorine and fluorine, each varying from 0 to 6 atoms inclusive, in the ethane structure, are illustrated. For purposes of simplicity this chart shows the fluorochloroalkanes empirically, as it has been found that with all the certain compounds used in practical operations, under this invention and as specified herein, the characteristics of the several isomers are so nearly the same that any of the several isomers will give substantially the same desirable results in practical printing operations.

In this chart, the top intersection of the equilateral triangle marked "Hydrogen," represents complete saturation with hydrogen, that is, represents the compound ethane (C_2H_6). The right hand corner represents complete saturation with chlorine, that is the compound hexachloroethane (C_2Cl_6). The left hand corner represents complete saturation with fluorine, i. e., hexafluoroethane (C_2F_6). The remaining intersections show all the intermediate combinations of the three variables with C_2. Thus all these compounds which are indicated on the chart by the numbers from 1 to 28 placed at the intersections are as follows:

1. C_2H_6, ethane
2. C_2ClH_5, monochloro ethane
3. $C_2Cl_2H_4$, dichloro ethane
4. $C_2Cl_3H_3$, trichloro ethane
5. $C_2Cl_4H_2$, tetrachloro ethane
6. C_2Cl_5H, pentachloro ethane
7. C_2Cl_6, hexachloro ethane
8. C_2FCl_5, monofluoro pentachloro ethane
9. $C_2F_2Cl_4$, difluoro tetrachloro ethane
10. $C_2F_3Cl_3$, trifluoro trichloro ethane
11. $C_2F_4Cl_2$, tetrafluoro dichloro ethane
12. C_2F_5Cl, pentafluoro monochlor ethane
13. C_2F_6, hexafluoro ethane
14. C_2F_5H, pentafluoro ethane
15. $C_2F_4H_2$, tetrafluoro ethane
16. $C_2F_3H_3$, trifluoro ethane
17. $C_2F_2H_4$, difluoro ethane
18. C_2FH_5, monofluoro ethane
19. C_2FClH_4, monofluoro monochloro ethane
20. $C_2F_2ClH_3$, difluoro monochloro ethane
21. $C_2FCl_2H_3$, monofluoro dichloro ethane
22. $C_2F_3ClH_2$, trifluoro monochloro ethane
23. $C_2F_2Cl_2H_2$, difluoro dichloro ethane
24. $C_2FCl_3H_2$, monofluoro trichloro ethane
25. C_2F_4ClH, tetrafluoro monochloro ethane
26. $C_2F_3Cl_2H$, trifluoro dichloro ethane
27. $C_2F_2Cl_3H$, difluoro trichloro ethane
28. C_2FCl_4H, monofluoro tetrachloro ethane

The more highly fluorinated the compound the less toxic it becomes, as apparently the toxicity decreases as the chlorine to fluorine ratio decreases. The higher the ratio of fluorine to chlorine the lower the toxicity. In actual operations it has been found that at least two fluorine atoms should be present to insure completely adequate non-toxicity. Moreover, as chlorine atoms are successively substituted by fluorine atoms in the molecule, the boiling point drops. The fluorine atom appears to influence the boiling point to about the same degree as would an hydrogen atom in the same position. From this discovery it is possible to predict, at least in an approximate manner, about what the boiling point of any fluorochloroalkane will be, knowing the boiling points of the corresponding hydrocarbon and that of the corresponding completely chlorinated material, and as it has been discovered that the volatility of these certain specified fluorochloroalkanes is higher than that of the hydrocarbon of corresponding boiling point, suitable allowance can be made in selection to give comparable press conditions.

I have found that many of the fluorochloroalkanes are of such character that they can be used as a rotogravure solvent to give suitable printing characteristics but that compounds with relatively few hydrogen atoms are to be desired for the reason that they are less inflammable and for very desirable commercial results a ratio of at least one halogen to two hydrogens, so far, has been found desirable. In general the derivatives of ethane, propane and butane, i. e., those compounds having 2 to 4 carbon atoms inclusive, appear to be most suitable, not only in yielding compounds of suitable boiling points and evaporation characteristics, but also because the non-inflammability characteristic of the compounds in the selected range tends to be less as the number of carbon atoms and accompanying hydrogen atoms increases, unless the hydrogen atoms are almost completely substituted by halogens, in which case the boiling points are in general too high for practical use under present printing conditions.

Thus some fluorochloroalkanes other than those so far found commercially usable may be suitable in rotogravure inks of special characteristics. Those most useful under present printing conditions, in which solvents are used having boiling points varying from 40° C. to 200° C., are the

specified ethane and propane derivatives. Illustrative of such solvents are those of the ethane series lying in a restricted portion of the illustrated chart, embracing the area having 2 or more fluorine atoms and less than 4 hydrogen atoms and indicated by the enclosing dotted line. This gives the desired non-toxicity and non-inflammability, and the number of fluorine atoms is selected so as to yield a compound of the desired boiling point. Thus of the substituted ethanes, the difluoro dichloro (23), difluoro trichloro (27), and difluoro tetrachloro (9) ethanes are all suitable; as is also the trifluoro trichloro (10) ethane. The trifluoro dichloro ethane (26), which has a boiling point of approximately 28° C., would be suitable for a very "fast" ink, i. e., a very rapidly evaporating ink; and difluoro monochloro ethane (20), which has a boiling point of approximately 35° C., would also be useful for an ink somewhat faster than those more generally used. These, like the remaining more highly fluorinated compounds, might be used if suitable cooling or refrigeration should be resorted to during printing operations.

Likewise similar propane and butane derivative charts could be evolved mathematically setting out all the theoretically possible empirical compounds. And in these also, the compounds of intermolecular relationship giving the desired characteristics for practically usable inks, would be similarly restricted, and where the practically negligible non-toxicity and non-inflammability are desired the compounds would have at least 2 fluorine atoms and not more than 5 hydrogen atoms for propane and 6 hydrogen atoms for butane. Proper substitution compounds within the present rotagravure printing solvent boiling point limits referred to as described for propane include the following:

Difluoro monochloro propane
Difluoro dichloro propane
Difluoro trichloro propane
Difluoro tetrachloro propane
Difluoro pentachloro propane
Difluoro hexachloro propane
Trifluoro dichloro propane
Pentafluoro trichloro propane
Trifluoro trichloro propane
Trifluoro tetrachloro propane
Trifluoro pentachloro propane
Tetrafluoro dichloro propane
Tetrafluoro trichloro propane
Tetrafluoro tetrachloro propane
Pentafluoro dichloro propane

which have such volatility, and the other desirable characteristics described, that they will make practical, satisfactory inks when admixed, alone or blended, as described. The volatility of the trifluoro monochloro, the tetrafluoro monochloro, the pentafluoro monochloro, the hexafluoro monochloro, the hexafluoro dichloro, and the heptafluoro monochloro propanes prevents their use under present printing operations; but if suitable refrigeration or other preventative of too ready evaporation should be provided these too might be used, as well as the derivatives containing only fluorine and hydrogen, i. e., no chlorine provided the hydrogen is not present to the extent of more than 5 atoms. Such illustrative charts for propane and butane are thought unnecessary for purposes of description and understanding of the invention, suitable non-inflammable and non-toxic compounds of suitably selected boiling points being readily determined from the above data which may be easily applied in use by the formula $C_nH_pF_xCl_y$; wherein n is 2 to 4 inclusive; x is 2 to 10 inclusive; y is 0 to 8 inclusive; and p is determined by

$$\frac{x+y}{p}$$

to be not less than one-half, and in which the sum of p, x, and y is always equal to $2n+2$.

Certain similar selections of usable compounds can be made from the higher homologs, having regard for the non-toxic, non-inflammable and boiling point characteristics as indicated.

The inflammability characteristics of some of the common rotogravure solvents are listed below in the table.

TABLE

Flash points of rotagravure solvents and solvent mixtures

Solvent	Percent by weight	Flash point, °F.
Benzol		1
Toluol		40
V. M. & P. naphtha		20–45
Methyl ethyl ketone		30
Ethyl alcohol		55
Ethyl acetate		24
Isopropyl alcohol		53
Petrolene		−4
Difluoro dichloro ethane		None
Difluoro tetrachloro ethane		None
Difluoro trichloro ethane		None
Monofluoro trichloro ethane		None
Difluoro pentachloro propane		None
Textile spirits	[1] 75	−18
Methyl ethyl ketone	25	
Difluoro trichloro ethane	30.9	None
Difluoro tetrachloro ethane	12.7	
Trifluoro tetrachloro propane	35.1	
V. M. & P. naphtha	21.3	
Difluoro trichloro ethane	40.0	None
Difluoro tetrachloro ethane	12.9	
Trifluoro tetrachloro propane	23.8	
V. M. & P. naphtha	23.3	

[1] This mixture is a widely used commercial rotogravure solvent mixture.

It will be observed from the table that the fluorochloroalkanes have no flash point and will not burn. "Petrolene," on the other hand, which is an aliphatic hydrocarbon mixture having a boiling range of about 142° F. to 202° F., and commonly used in rotogravure inks, has the extremely low flash point of −4° F., that is, it will flash at a temperature even below freezing. Other materials show somewhat higher flash points but are decidedly dangerous from the standpoint of fire hazard in being below the limit of 27° C. specified by the Interstate Commerce Commission as requiring a red label for shipment in interstate commerce. The inflammability data is given in the form of flash points determined according to the A. S. T. M. method D 56–36 by means of the Tagliabue closed cup apparatus.

A single fluorochloroalkane can be used as the entire solvent component of my inks, as illustrated below by Example I, or several may be blended together as in Example II, to produce the desired evaporation range curve as is customary in solvent blending. In this connection it is desirable to so blend the solvent constituents of the inks as printed, that the combined evaporation characteristics will be such that a preponderance of the solvent evaporates relatively quickly to insure rapid drying, but that an adequate amount of active solvent is present at all stages of the evaporation, and particularly toward the end, to maintain the resinous and bituminous constituents in solution and the ink sufficiently fluid to insure adequate flow and a resulting good "lay" of the ink on the paper.

One or more of the fluorochloralkanes may be blended together or with other solvents, as illus-

trated in the table and in Examples III, IV and V, and when so blended in proper proportions will impart their characteristics of non-inflammability and non-toxicity to the degree in which they are used.

Example II illustrates the use of several fluorochloroalkanes blended with respect to boiling points and exaporation rates to give the desired smooth evaporation curve, and Examples III, IV and V illustrate a compound blend of fluoroalkanes and another solvent to have such characteristic. The proportions required to give the desired increase in flash point of the non-fluorochloroalkane may be readily determined. For example, the V. M. & P. naphtha of Examples III and IV, which is essentially a diluent, has a boiling range of approximately 100–160° C., while the approximate boiling points of the fluorochloroalkanes used are—difluoro trichloro ethane 72° C., difluoro tetrachloro ethane 92° C., trifluoro tetrachloro propane 130° C. Thus the fluorochloroalkane content of the ink is adequate at all times during the evaporation to maintain the resinous or bituminous material in solution, while the naphtha insures adequate fluidity of the material throughout its range of evaporation.

I have discovered that many solvent combinations which flash below the danger point, can be raised to comparative safety by the use of relatively small proportions of the fluorochloroalkanes. When the fluorochloroalkanes are used alone or in proper admixture with each other, or in proper relative admixture with other materials, as rotogravure ink solvents they impart their high degree of non-inflammability and non-toxicity to the ink. The fluorochloroalkanes are non-toxic even in high concentrations. No danger to life is observed except as concentrations may be so high as to leave serious doubt as to whether the effect is due to oxygen deficiency resulting from the displacement of air by the fluorochloro compound rather than to the fluorochloro compound itself. From the practical viewpoint of health hazards these compounds, as used in inks under the present invention, are entirely non-toxic.

Formulas for rotogravure inks suitable from the point of view of non-inflammability and non-toxicity and having very satisfactory operating characteristics, are given below.

EXAMPLE I.—BLACK INK

	Percent by weight
Difluoro trichloro ethane	69.00
Asphalt	10.00
Limed rosin	2.00
Gilsonite	7.50
Aluminum stearate	0.50
Carbon black	2.50
Lamp black	0.25
Cumar resin	3.00
Blue toner	0.50
China clay	4.75
	100.00

EXAMPLE II.—BROWN INK

	Percent by weight
Difluoro trichloro ethane	39.00
Difluoro tetrachloro ethane	16.00
Trifluoro tetrachloro propane	26.00
Gilsonite	15.54
Para red pigment	.86
Clay	2.60
	100.00

EXAMPLE III.—BROWN INK

	Percent by weight
Difluoro trichloro ethane	32.50
Difluoro tetrachloro ethane	10.55
Trifluoro tetrachloro propane	19.35
V. M. & P. naphtha	19.10
Gilsonite	15.00
Para red pigment	.86
Clay	2.64
	100.00

EXAMPLE IV.—BLUE INK

	Percent by weight
Difluoro trichloro ethane	25.00
Difluoro tetrachloro ethane	10.30
Trifluoro tetrachloro propane	28.38
V. M. & P. naphtha	17.22
Batu resin	12.10
Synthetic resin (alkyd)	1.90
Milori blue pigment	3.20
Aluminum hydrate	1.90
	100.00

EXAMPLE V.—RED INK

	Percent by weight
Difluoro dichloro ethane	45.00
Difluoro tetrachloro ethane	10.00
Cellulose triacetate	10.00
Para red	8.00
Arochlor resin (chlorinated diphenyl)	4.00
Plasticizer	6.00
Leveling agent	7.00
Inert filler	10.00
	100.00

As pointed out above, these fluorochloroalkanes are excellent solvents, not only for the asphalts and gilsonites which are so widely used as binders in brown rotogravure inks, but also for a great many of the commonly available natural and synthetic resins, including rosin, damar, ester gums, alkyd, phenol-aldehyde, chlorinated diphenyls (Arochlors) and many others. The copals, shellac and vinyl resins, as well as some of the hard waxes such as carnauba wax are not soluble in the fluorochloroalkanes. Furthermore, the fluorochloroalkanes are excellent solvents for cellulose derivatives; and it has been discovered that they are excellent solvents for unhydrolyzed cellulose triacetate. This is a very non-inflammable cellulose derivative, which is practically insoluble in most of the common organic solvents. The usual commercial cellulose acetates are prepared by forming cellulose triacetate and then hydrolyzing this initially formed cellulose triacetate so as to improve, and give it commercially usable, solubility characteristics. I have discovered that these fluorochloroalkanes will act as excellent solvents for this initially formed cellulose triacetate, and as a result this relatively inexpensive grade of cellulose triacetate, can be used and put into solution without the expense and difficulties in manufacture which are incident to the treatments heretofore given to change it from its initial formation, and the resulting solution, as a composition of matter, can be used in varying proportions as binders, coatings, etc., in fields and for purposes other than the preparation of inks or binders and solvents therefore.

While the composition herein described constitutes a preferred embodiment of the invention, it

is to be understood that the invention is not limited thereto and that changes may be made therein without departing from the scope of invention which is defined in the appended claims.

What is claimed is:

1. A non-toxic, non-inflammable rotogravure ink comprising a pigment, and a binder material dissolved in a solvent comprising as an essential major component a fluorochloroalkane having a boiling point within the range of substantially 40° to 200° C., the solvent being present in major proportion forming an ink having solvent release and high speed of evaporation providing adequate flow and lay of the ink on the paper.

2. A non-toxic, non-inflammable rotogravure ink comprising a pigment, and a binder material selected from the group consisting of natural resins, synthetic resins, asphalt, gilsonite, and cellulose acetate, dissolved in a solvent comprising a fluorochloroalkane containing more than one and less than five carbon atoms, the solvent being present in the ink in major proportions forming an ink having high speed of evaporation and solvent release suitable for rotogravure printing.

3. A non-toxic, non-inflammable rotogravure ink comprising a pigment, and a binder dissolved in a fluorochloroalkane solvent having at least one chlorine atom, at least two fluorine atoms and a ratio of halogen to hydrogen of at least 1 to 2, the solvent being present in the ink in major proportion providing an ink having a boiling point within the range of substantially 40° to 200° C. and high speed of evaporation and good solvent release.

4. A non-toxic, non-inflammable rotogravure ink comprising a pigment, and a binder dissolved in a solvent having the formula $C_nH_yF_xCl_y$; where n is 2 to 4 inclusive; x is 2 to 10 inclusive; y is 0 to 8 inclusive; and p is determined by

$$\frac{x+y}{p}$$

to be not less than one-half, and in which the sum of p, x, and y is always equal to $2n+2$, the solvent being present in major proportion forming an ink having boiling point, volatility, high speed of evaporation and solvent release characteristics adequate for rotogravure printing.

5. A rotogravure ink as defined in claim 1 in which the fluorochloroalkane solvent has two carbon atoms, not less than two fluorine atoms, and less than four hydrogen atoms.

6. A rotogravure ink as defined in claim 1 in which the fluorochloralkane solvent has three carbon atoms, not less than two fluorine atoms, and less than five hydrogen atoms.

7. A rotogravure ink as defined in claim 1 in which the fluorochloralkane solvent has four carbon atoms, not less than two fluorine atoms, and less than six hydrogen atoms.

8. A non-toxic, non-inflammable rotogravure ink comprising a pigment and a binder material dissolved in a solvent comprising a fluorochloroalkane selected from the group consisting of difluorodichloroethane, difluorotrichloroethane, difluorotetrachloroethane, and trifluorotrichloroethane, and having a boiling point within the range of substantially 40° to 200° C., the solvent being present in the ink in major proportion forming an ink having volatility, solvent release, and speed of evaporation characteristics suitable for rotogravure printing.

9. A non-toxic and non-inflammable solvent mixture adapted for dissolving a pigment and a binder to form rotogravure inks comprising a mixture of fluorochloroalkanes selected to give a blend having a substantial evaporation range such that a preponderant portion of the solvent evaporates more quickly than the minor portion whereby rapid drying is secured, but delay in the evaporation of the minor fraction insures adequate flow and lay of the ink upon the paper as with other known inks of equivalent characteristics as to printing, said solvent mixture comprising a mixture of fluorochloroalkanes each having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2.

10. A non-toxic solvent mixture adapted for dissolving a pigment and a binder to form rotogravure inks comprising a major fraction including a fluorochloroalkane having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2, and a minor proportion of other aliphatic solvent material having a boiling range of approximately 100–160° C. blended with said major fraction to give a smooth evaporation curve for proper flow and lay of the ink upon the paper, the fluorochloroalkane fraction having a boiling range lower than that of said other aliphatic solvent material, and said composite solvent having a flash point of not less than 27° C., determined as described.

11. A non-toxic, non-inflammable rotogravure ink comprising a pigment and a binder dissolved in a solvent comprising a mixture of fluorochloroalkanes selected to give a blend having a substantial evaporation range such that a preponderant portion of the solvent evaporates more quickly than the minor portion when the ink is printed whereby rapid drying is secured, but delay in evaporation of the minor fraction insures adequate flow and lay of the ink on the paper, as with other known inks of equivalent characteristics as to printing, said solvent comprising a mixture of fluorochloroalkanes each having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2.

12. A non-toxic, non-inflammable rotogravure ink comprising a pigment and a binder dissolved in a solvent comprising a mixture of fluorochloroalkanes selected to give a blend having a substantial evaporation range such that a preponderant portion of the solvent evaporates more quickly than a minor portion whereby rapid drying is secured, but delay in the evaporation in the minor fraction insures adequate flow and lay of the ink on the paper, as with other known inks of equivalent characteristics as to printing, said solvent comprising a mixture of fluorochloroalkanes each having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2, said binder being selected from the group consisting of natural resins, synthetic resins, asphalt, gilsonite and cellulose acetate.

13. A non-toxic, non-inflammable rotogravure ink comprising a pigment and a binder dissolved in a solvent comprising a major fraction including at least one fluorochloroalkane having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2, and a minor fraction of other aliphatic solvent material which is more inflammable than a fluorochloroalkane, said other sol-

vent material having a boiling range of approximately 100–160° C., the fluorochloroalkane fraction having a boiling range lower than that of the other said aliphatic solvent and effective with respect to the normal flash point of said other solvent to provide a composite having a flash point of not less than 27° C., determined as described.

14. As a composition of matter, unhydrolized cellulose triacetate as formed as a separated reaction product dissolved in a non-toxic, non-inflammable solvent comprising a fluorochloroalkane.

15. As a composition of matter, unhydrolized cellulose triacetate as formed as a separated reaction product dissolved in a non-toxic, non-inflammable solvent comprising a fluorochloroalkane having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2.

16. A non-toxic, non-inflammable rotogravure ink comprising a binder dissolved in a solvent comprising at least one fluorochloralkane having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2, said binder comprising unhydrolized cellulose triacetate soluble directly in said solvent, and a coloring agent such as a pigment.

17. A non-toxic, non-inflammable rotogravure ink comprising a binder material consisting of unhydrolized cellulose triacetate dissolved directly in a solvent comprising a fluorochloroalkane having a boiling point within the range of substantially 40° to 200° C.

18. A non-toxic rotogravure ink comprising a binder material, a coloring material and a fluorochloroalkane solvent component, said fluorochloroalkane having a flash point above 27° C. and a boiling point within the range of substantially 40° to 200° C.

CLARENCE E. IRION.

CERTIFICATE OF CORRECTION.

Patent No. 2,381,753. August 7, 1945.

CLARENCE E. IRION.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 18, in the Table, second column thereof, opposite "Benzol" for the numeral "1" read --12--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of November, A. D. 1945.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

vent material having a boiling range of approximately 100–160° C., the fluorochloroalkane fraction having a boiling range lower than that of the other said aliphatic solvent and effective with respect to the normal flash point of said other solvent to provide a composite having a flash point of not less than 27° C., determined as described.

14. As a composition of matter, unhydrolized cellulose triacetate as formed as a separated reaction product dissolved in a non-toxic, non-inflammable solvent comprising a fluorochloroalkane.

15. As a composition of matter, unhydrolized cellulose triacetate as formed as a separated reaction product dissolved in a non-toxic, non-inflammable solvent comprising a fluorochloroalkane having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2.

16. A non-toxic, non-inflammable rotogravure ink comprising a binder dissolved in a solvent comprising at least one fluorochloralkane having from two to four carbon atoms, not less than two fluorine atoms, and a ratio of halogen to hydrogen of at least 1 to 2, said binder comprising unhydrolized cellulose triacetate soluble directly in said solvent, and a coloring agent such as a pigment.

17. A non-toxic, non-inflammable rotogravure ink comprising a binder material consisting of unhydrolized cellulose triacetate dissolved directly in a solvent comprising a fluorochloroalkane having a boiling point within the range of substantially 40° to 200° C.

18. A non-toxic rotogravure ink comprising a binder material, a coloring material and a fluorochloroalkane solvent component, said fluorochloroalkane having a flash point above 27° C. and a boiling point within the range of substantially 40° to 200° C.

CLARENCE E. IRION.

CERTIFICATE OF CORRECTION.

Patent No. 2,381,753. August 7, 1945.

CLARENCE E. IRION.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 18, in the Table, second column thereof, opposite "Benzol" for the numeral "1" read --12--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of November, A. D. 1945.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.