(54) Title: SUBCRITICAL COMPRESSED FLUIDS AS VISCOSITY REDUCING DILUENTS FOR TRANSPORTABLE COMPOSITIONS

(57) Abstract

Processes are disclosed for reducing the viscosity of compositions containing one or more polymeric compounds so as to make them transportable by adding a subcritical compressed fluid, which fluid is a gas at standard conditions of 0 °C and one atmosphere pressure.

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Title: SUBCRITICAL COMPRESSED FLUIDS AS
          VISCOSITY REDUCING DILUENTS FOR
          TRANSPORTABLE COMPOSITIONS

Related Patent Applications

This application contains subject matter
related to U.S. Patent Application No. 418,820, filed
October 4, 1989, now U.S. Patent No. 4,923,720,
issued May 8, 1990, and U.S. Patent Application
Serial No. 327,273, filed March 22, 1989.

Field of the Invention

This invention, in general, pertains to the
field of reducing the viscosity of a composition
containing one or more polymeric compounds so as to
make it transportable. Typically, the composition
will be a coating composition for coating
substrates. More specifically, the present invention
relates to the use of subcritical compressed fluids,
such as subcritical compressed carbon dioxide or
subcritical compressed nitrous oxide, as a viscosity
reduction diluent and an atomization agent or
enhancer for spraying coating compositions.

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Background of the Invention

Prior to the inventions described in the aforementioned related patent applications, the liquid spray application of coatings, such as paints, lacquers, enamels and varnishes, was effected solely through the use of organic solvents as viscosity reduction diluents. However, because of increased environmental concern, efforts have been directed to reducing the pollution resulting from painting and finishing operations. For this reason, there has been a great deal of emphasis placed on the development of new coatings technologies that diminish the emission of organic solvent vapors. A number of technologies have emerged as having met most but not all of the performance and application requirements, and at the same time meeting emission requirements and regulations. They are: (a) powder coatings, (b) water-borne dispersions, (c) water-borne solutions, (d) non-aqueous dispersions, and (e) high-solids coatings. Each of these technologies has been employed in certain applications and each has found a niche in a particular industry. However, at the present time, none has provided the performance and application properties that were initially expected.

Powder coatings, for example, while providing ultra low emission of organic vapors, are generally characterized as having poor gloss or good gloss with heavy orange peel, poor distinctness of image gloss (DOI), and poor film uniformity.

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Moreover, to obtain even these limited performance
properties generally requires excessive film
thickness and/or high curing temperatures.
Pigmentation of powder coatings is often difficult,
requiring at times milling and extrusion of the
polymer-pigment composite mixture followed by
cryogenic grinding. In addition, changing colors of
the coating often requires its complete cleaning,
because of dust contamination of the application
equipment and finishing area.

Water-borne coatings, on the other hand, are
very difficult to apply under conditions of high
relative humidity without serious coating defects.
These defects result from the fact that under
conditions of high humidity, water evaporates more
slowly than the organic cosolvents of the coalescing
aid, and as might be expected in the case of aqueous
dispersions, the loss of the organic
cosolvent/coalescing aid interferes with film
formation. Poor gloss, poor uniformity, and pin
holes unfortunately often result. Additionally,
water-borne coatings are not as resistant to
corrosive environments as are more conventional
solvent-borne coatings.

Coatings applied with organic solvents at
high solids levels avoid many of the pitfalls of
powder and water-borne coatings. However, in these
systems, the molecular weight of the polymer has been
decreased and reactive functionality incorporated or
increased therein so that further polymerization and

crosslinking can take place after the coating has
been applied. It has been hoped that this type of
coating will meet the ever increasing regulatory
requirements and yet meet the most exacting coatings
performance demands. However, there is a limit as to
the ability of this technology to meet the
performance requirements of a commercial coating
operation. Present high-solids systems have
difficulty in application to vertical surfaces
without running and sagging of the coating. If they
possess good reactivity, they often have poor shelf
and pot life. However, if they have adequate shelf
stability, they cure and/or crosslink slowly or
require high temperature to effect an adequate
coating on the substrate.

Clearly, what was needed was an
environmentally safe, non-polluting diluent that can
be used to thin very highly viscous polymer and
coatings compositions to liquid spray application
consistency. Such a diluent would allow utilization
of the best aspects of organic solvent-borne coatings
applications and performance while reducing the
environmental concerns to an acceptable level. Such
a coating system could meet the requirements of
shop-applied and field-applied liquid spray coatings
as well as factory-applied finishes and still be in
compliance with environmental regulations.

Such a needed diluent was indeed found and
is discussed in the aforementioned related patent
which teaches, among other things, the utilization of

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supercritical fluids, such as supercritical carbon
dioxide fluid, as diluents in highly viscous organic
solvent-borne and/or highly viscous non-aqueous
dispersions coatings compositions to dilute these
compositions to application viscosity required for
liquid spray techniques.

As used herein, it will be understood that a
"supercritical fluid" is a material which is at a
temperature and pressure such that it is at, above,
or slightly below its "critical point". As used
herein, the "critical point" is the transition point
at which the liquid and gaseous states of a substance
merge into each other and represents the combination
of the critical temperature and critical pressure for
a given substance. The "critical temperature", as
used herein, is defined as the temperature above
which a gas cannot be liquified by an increase in
pressure. The "critical pressure", as used herein,
is defined as that pressure which is just sufficient
to cause the appearance of two phases at the critical
temperature.

Also as used herein, it will be understood
that a "subcritical fluid" is a material which is at
a temperature and/or pressure such that it is below
its critical point. Such a subcritical fluid may be
(i) below its critical temperature while being above
its critical pressure, or (ii) below its critical
pressure while being above its critical temperature,
or (iii) below both its critical temperature and
critical pressure.

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While the utilization of supercritical
fluids as viscosity reducing diluents in coating
applications has met with much success and is
effectively able to accomplish the primary objective
of reducing the emission of volatile organic
compounds into the atmosphere while simultaneously
providing the stringent performance characteristics
of the applied coating that is required by the
coatings industry, a desire has nevertheless arisen
to determine whether such viscosity reducing diluent
effects can be obtained with suitable materials at
conditions which are below their critical point,
i.e., with subcritical fluids. In particular, this
desire has been generated by the realization that
there are coating materials which may contain
components that are highly temperature sensitive,
such as highly reactive cross-linking coating systems
and two-package coating systems that are employed in
high-solids coatings. As such, it may be undesirable
to subject such components to the temperatures
required to keep the viscosity reducing supercritical
fluid in its supercritical state. By spraying at
significantly lower temperature, it may be possible
to spray a two-package coating using a conventional
single-feed coating system instead of having to feed
the two reactive components separately as required at
elevated spray temperatures. In cross-linking
coating systems, the undesirable increase in spray
viscosity that results from premature reaction in the
heated spray equipment can therefore be avoided or
minimized.

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Furthermore, it is common for sprays with supercritical fluids to be heated to relatively high temperatures, typically 50 to 60 C or higher, to offset the cooling effect that occurs as the supercritical fluid expands from the spray as a free gas. This requires either the use of a circulating flow of the heated spray mixture, which is undesirable for spray operations that use color change or highly reactive coating systems, due to increased volume and residence time, or the use of a specially heated and thermostated spray gun and feed line in order to maintain the proper spray temperature at all times including at start-up. This increases the amount of equipment that must be operated and maintained in the spray operation, which increases equipment and labor costs and makes the operation more susceptible to interruptions due to equipment failure or loss of temperature control. Still further, at elevated temperatures, an excessive proportion of supercritical fluid above its solubility limit is avoided so as to prevent a portion of the organic solvent, which has high vapor pressure at elevated temperature, to be extracted from the liquid coating phase into a second supercritical fluid phase. This would produce poor quality coatings that do not flow out properly due to the loss of the extracted solvent, which escapes directly into the atmosphere with the supercritical fluid. Because spraying with supercritical fluids generally uses a concentration of the supercritical fluid that is at or just below its solubility limit, the proportion is carefully controlled. At low spray

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temperatures, however, the organic solvents are much
less volatile and therefore much less would be
extracted from the liquid coating phase.
Accordingly, advantages such as improved atomization
that can result from a significant excess of
subcritical fluid above the solubility limit can be
utilized.

So too, generally depending on the
particular coating composition to be sprayed, at the
typically higher pressures needed to maintain the
viscosity reducing supercritical fluid in its
supercritical state, i.e., above its critical
pressure, and at the typically still higher pressures
required to obtain high solubility of the
supercritical fluid at the elevated temperatures,
more wear and tear may be experienced on the spray
coating equipment, particularly the spray gun nozzle
tips. Moreover, there is a general desire,
particularly for safety reasons, to work with a
process at a pressure which is as low as possible
while still realizing the overall benefits of such a
process.

Lower pressures also produce a lower
velocity spray, which is advantageous for obtaining
higher transfer efficiency in depositing the coating
composition onto a substrate and in particular for
making electrostatic deposition more effective.
Lower spray velocity can also improve coating quality
by reducing the amount of fine air bubbles that
become entrapped in the liquid coating as the spray

strikes the substrate, which may cause undesirable
haze to occur in clear coatings and may promote
solvent popping during baking. Lower pressures also
make it possible to obtain lower spray application
rates without having to use extremely small orifice
sizes that are susceptible to becoming plugged and
are difficult to manufacture. There is also a
general desire to spray at the lower pressures at
which air-assisted airless spraying is practiced,
which are generally below supercritical fluid
pressures.

SUMMARY OF THE INVENTION

By virtue of the present invention, the
above needs have now been met. Processes have now
been discovered which are able to provide a viscosity
reducing effect and enhanced atomization with a
suitable environmentally acceptable material which is
at subcritical conditions thereby still minimizing
the use of environmentally undesirable organic
solvents and simultaneously reducing the pressure
and/or temperature needed to achieve such a viscosity
reducing diluent effect.

In particular, we have discovered that
subcritical compressed fluids may be utilized as
viscosity reducing diluents and as atomization
enhancing agents for compositions containing one or
more polymeric compounds, such as coating
compositions, wherein the subcritical compressed

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fluid is a gas at standard conditions of 0°C and one atmosphere pressure (STP), provided that such compositions contain one or more polymeric compounds which have a number-average molecular weight of less than about 5,000. We have further discovered that the coating compositions may also contain one or more polymeric compounds having higher number-average molecular weights provided that at least 75 weight percent of the total weight of all polymeric compounds has a weight-average molecular weight of less than about 20,000. Our attempts to spray liquid mixtures using subcritical compressed fluids were generally unsuccessful until we discovered that the molecular weight of the polymers present in the compositions was a critical parameter, as will be discussed more fully below.

As used herein, a "compressed fluid" is a subcritical fluid which may be in its gaseous state, its liquid state, or a combination thereof depending upon the particular temperature and pressure to which it is subjected upon admixture with the composition which is to have its viscosity reduced and the vapor pressure of the fluid at that particular temperature, but which is in its gaseous state at standard conditions of 0°C and one atmosphere (STP).

Also as used herein, the phrases "coating composition" and "coating formulation" are understood to mean conventional coating formulations that have no subcritical compressed fluid admixed therewith. Also as used herein, the phrases "liquid mixture",

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"spray mixture", and "admixed coating composition"
are meant to include an admixture of a coating
composition or coating formulation with at least one
subcritical compressed fluid.

It is understood, of course, that the term
"coating composition" is not limited to coatings that
are only used to protect and/or enhance the
appearance of a substrate or which is decorative,
such as paints, lacquers, enamels, and varnishes.
Indeed, the coating composition may provide a coating
which acts as an adhesive, or which is a release
agent; a lubricant; a cleaning agent; or the like.
Such coating compositions may also include those that
are typically utilized in the agricultural field in
which fertilizers, weed killing agents, and the like,
are dispensed. Such coating compositions may also
include those that are used to coat agricultural
products such as fruits and vegetables or to coat
pharmaceutical or medicinal products such as pills
and tablets. The specific nature of the coating
composition is not critical to the present invention
provided that it can be admixed with the subcritical
compressed fluid and then be sprayed.

More specifically, in its broadest
embodiment, the process of the present invention is
directed to a process for reducing the viscosity of a
composition containing one or more liquid polymeric
compounds to make it transportable comprising forming
a liquid mixture in a closed system comprising:

a)   a composition containing a first set of
at least one or more liquid polymeric compounds
wherein the number-average molecular weight of the
one or more liquid polymeric compounds is less than
about 5,000; and

b)   at least one subcritical compressed
fluid in at least an amount which when added to (a)
is sufficient to render the viscosity of said mixture
to a point suitable for being transportable, wherein
the subcritical compressed fluid is a gas at standard
conditions of $0^{o}C$ and one atmosphere (STP).

In a further embodiment, yet additional one
or more polymeric compounds may be provided in the
composition, if desired, having number-average
molecular weights which may be greater than 5,000
provided, however, that at least about 75 weight
percent of all of the polymeric compounds contained
in the composition in the aggregate have a
weight-average molecular weight of less than about
20,000.

As used herein, the term "transportable" is
meant to provide the liquid mixture with a viscosity
such that it is capable of being fasciley conveyed
from one point to another by any means, such as by
pumping, passing through a pipe or a conduit, passing
through an orifice, being able to be sprayed, and the
like. It is not meant to merely taking the liquid
mixture and placing it in a container such that the
conveyance of the container makes the liquid mixture
transportable.

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In a more preferred embodiment, the above noted process also includes the presence of an active solvent in the liquid mixture so as to aid in the reduction of the viscosity and therefore does not require the use of liquid polymers. Polymers other than liquid polymers may also be utilized.

In yet another embodiment of the present invention, a process for the liquid spray application of coatings to a substrate is disclosed, which comprises:

a)   forming a liquid mixture in a closed system, said liquid mixture comprising:

i)   at least one or more liquid polymeric compounds capable of forming a coating on a substrate wherein the number average molecular weight of the one or more liquid polymeric compounds is less than about 5,000; and

ii)   at least one subcritical compressed fluid in at least an amount which when added to (i) is sufficient to render the viscosity of said mixture to a point suitable for spray application, wherein the subcritical compressed fluid is a gas at standard conditions of 0°C and one atmosphere (STP); and

b)   spraying said liquid mixture onto a substrate to form a liquid coating thereon having substantially the composition of the said coating formulation.

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Here again, in a further embodiment, yet
additional one or more polymeric compounds may be
provided in the composition, if desired, having
number-average molecular weights which may be greater
than 5,000 provided, however, that at least about 75
weight percent of all of the polymeric compounds
contained in the composition in the aggregate have a
weight-average molecular weight of less than about
20,000. Polymers other than liquid polymers may also
be utilized.

In an alternative embodiment of this liquid
spray application process, at least one active
solvent is added in which one or more of the
polymeric compounds are at least partially soluble
and which is at least partially miscible with the
subcritical compressed fluid. In a preferred
embodiment, the subcritical compressed fluid is
carbon dioxide. Liquid polymeric compounds are also
not required in the alternative embodiment.

Although clearly applicable to the
application of any coating composition, the present
invention is particularly useful in the application
of high-solids coatings. Coating formulators and
applicators face the difficult task of further
reducing organic solvent emissions from spray
operations while maintaining the advantages of
organic solvent-borne coatings, namely, superior
appearance, performance, convenience, and economics.
Over the years, solvent emissions have been reduced
by formulating coatings with less organic solvent and

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consequently higher solids levels. This has been
accomplished by (1) decreasing polymer molecular
weights to maintain low viscosity for spraying and
(2) increasing polymer reactive functionality to
obtain a solid coating after application. However,
this technique has generally approached the limit to
which the solid levels can be increased without
coating quality deteriorating further and becoming
unacceptable. High-solids coatings generally have
problems of running and sagging, cratering and pin
holing, poor shelf and pot life, and cross-linking
that is slow or requires high temperatures, all due
to the use of very low molecular weight polymers.

By means of the present invention, the use
of subcritical compressed fluids in the manner
described herein can replace the fast solvents of the
high-solids coatings while retaining the benefits of
organic solvent-borne coatings. Thus, high quality
coatings can be reformulated with even higher solids
levels, attaining viscosities in the range of from
about 200 to about 3,000 cps. (All viscosities
referred to herein have been measured at a standard
temperature and pressure of 25°C and one atmosphere
pressure, unless noted otherwise.) For high-solids
coatings that already meet volatile organic compound
regulatory requirements, replacing the fast solvents
with the subcritical fluids allows the high-solids
coatings to be reformulated with a correspondingly
higher content of slow, coalescing solvents.
Consequently, the molecular weights of the polymeric
components may be increased to regain more of the

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advantages of organic solvent-borne coatings, i.e.,
better appearance, performance, and pot life, and
shorter cure times at lower temperatures.

Brief Description of the Drawings

Figure 1 is a schematic diagram of an
embodiment of the present invention in which an
accurately proportioned mixture of subcritical
compressed carbon dioxide and coating formulation are
prepared in preparation for spraying.

Figure 2 is a schematic diagram of a more
preferred embodiment of the apparatus shown in Figure
1.

Figure 3 is a diagrammatic illustration of a
feathered decompressive spray pattern coating layer
obtained on a substrate when the coating mixture is
sprayed so as to obtain good atomization in
accordance with the objectives of the present
invention.

Figure 4 is a diagrammatic illustration of a
fishtail spray pattern coating layer which occurs
when spray conditions are such that a feathered
decompressive spray pattern is not obtained, such as
the concentration of subcritical compressed fluid
being too low in the spray mixture.

Figures 5a - 5f are photoreproductions of
actual atomized liquid sprays containing a feathered

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decompressive spray pattern in accordance with the
preferred spraying mode of the present invention.

Figures 6a - 6g are photoreproductions of
actual atomized liquid sprays containing a fishtail
liquid-film spray pattern for coating compositions
sprayed either without or with too little subcritical
compressed fluid.

Figure 7a - 7b are photoreproductions of
actual atomized liquid sprays showing the transition
from a feathered decompressive spray pattern to a
fishtail liquid-film spray pattern upon increase in
polymer molecular weight due to catalyzed reaction
over time.

Figure 8 is a diagram comparing temperature
profiles of sprays produced using supercritical
carbon dioxide with sprays produced using subcritical
compressed carbon dioxide with a feathered
decompressive spray or with a fishtail liquid-film
spray.

Figure 9 is a diagram showing carbon dioxide
solubility in a coating composition as a function of
pressure at constant temperature.

Figure 10 is a diagram showing viscosity
reduction of a coating composition with increasing
concentration of dissolved subcritical compressed
carbon dioxide.

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Detailed Description of the Invention

The present invention is not narrowly
critical to the type of coating composition that can
be sprayed provided that there is less than about 30%
by weight, preferably less than about 20% by weight
of water in the solvent fraction (as herein later
defined) of the composition and also provided that
the molecular weight of the polymeric constituents
present in the coating composition be within a
particular range, which was briefly discussed
earlier. Thus, essentially any coating composition
meeting the aforementioned water limit requirement
which is conventionally sprayed with an airless spray
technique and which also contains the molecular
weight requirements of its polymeric components may
also be sprayed by means of the preferred embodiments
of the present invention.

Generally, such coating compositions
typically include a solids fraction containing at
least one component which is capable of forming a
coating on a substrate, whether such component is an
adhesive, a paint, lacquer, varnish, mold release
agent, chemical agent, lubricant, protective oil,
non-aqueous detergent, or the like. Typically, at
least one component is a polymeric component which is
well known to those skilled in the coatings art.

The materials used in the solids fraction of
the present invention, such as the polymers,
generally must be able to withstand the temperatures

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and/or pressures which are involved when they are
ultimately admixed with the at least one subcritical
fluid. Such applicable polymers include
thermoplastic or thermosetting materials or may be
crosslinkable film forming systems.

In particular, the polymeric components
include vinyl, acrylic, styrenic, and interpolymers
of the base vinyl, acrylic, and styrenic monomers;
polyesters, oil-free alkyds, alkyds, and the like;
polyurethanes, two-package polyurethane, oil-modified
polyurethanes and thermoplastic urethanes systems;
epoxy systems; phenolic systems; cellulosic esters
such as acetate butyrate, acetate propionate, and
nitrocellulose; amino resins such as urea
formaldehyde, melamine formaldehyde, and other
aminoplast polymers and resins materials; natural
gums and resins; rubber-based adhesives including
nitrile rubbers which are copolymers of unsaturated
nitriles with dienes, styrene-butadiene rubbers,
thermoplastic rubbers, neoprene or polychloroprene
rubbers, and the like.

In addition to the polymeric compounds that
may be contained in the solids fraction, conventional
additives which are typically utilized in coatings
may also be used. For example, pigments, pigment
extenders, metallic flakes, fillers, drying agents,
anti-foaming agents, and anti-skinning agents,
wetting agents ultraviolet absorbers, cross-linking
agents, and mixtures thereof, may all be utilized in
the coating formulation to be sprayed by the methods
of the present invention.

In addition to the solids fraction, a
solvent fraction is also typically employed in the
coating compositions whether they be an adhesive
composition or a paint, lacquer, varnish, or the
like, or an agricultural spray, in order to act as a
vehicle in which the solid fraction is transported
from one medium to another. As used herein, the
solvent fraction is comprised of essentially any
active organic solvent and/or non-aqueous diluent
which is at least partially miscible with the solids
fraction so as to form either a solution, dispersion,
or suspension. As used herein, an "active solvent"
is a solvent in which the solids fraction is at least
partially soluble. The selection of a particular
solvent fraction for a given solids fraction in order
to form a specific coating formulation for
application by airless spray techniques is
conventional and well known to those skilled in the
art. In general, up to about 30% by weight of water,
preferably up to about 20% by weight, may also be
present in the solvent fraction provided that a
coupling solvent is also present in the formulation.
All such solvent fractions are suitable in the
present invention.

A coupling solvent is a solvent in which the
polymeric compounds used in the solids fraction is at
least partially soluble. Most importantly, however,
such a coupling solvent is also at least partially
miscible with water. Thus, the coupling solvent
enables the miscibility of the solids fraction, the
solvent fraction and the water to the extent that a

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single phase is desirably maintained such that the
composition may optimally be sprayed and a good
coating formed.

Coupling solvents are well known to those
skilled in the art and any conventional coupling
solvents which are able to meet the aforementioned
characteristics, namely, those in which the polymeric
components of the solid fraction is at least
partially soluble and in which water is at least
partially miscible are all suitable for being used in
the present invention.

Applicable coupling solvents which may be
used in the present invention include, but are not
limited to, ethylene glycol ethers; propylene glycol
ethers; chemical and physical combinations thereof;
lactams; cyclic ureas; and the like.

Specific coupling solvents (which are listed
in order of most effectiveness to least
effectiveness) include butoxy ethanol, propoxy
ethanol, hexoxy ethanol, isopropoxy 2-propanol,
butoxy 2-propanol, propoxy 2-propanol, tertiary
butoxy 2-propanol, ethoxy ethanol, butoxy ethoxy
ethanol, propoxy ethoxy ethanol, hexoxy ethoxy
ethanol, methoxy ethanol, methoxy 2-propanol, and
ethoxy ethoxy ethanol. Also included are lactams
such as n-methyl-2-pyrrolidone, and cyclic ureas such
as dimethyl ethylene urea.

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When water is not present in the coating
formulation, a coupling solvent is not necessary, but
may still be employed. Other solvents, particularly
active solvents, which may be present in typical
coating formulations and which may be utilized in the
present invention include ketones such as acetone,
methyl ethyl ketone, methyl isobutyl ketone, mesityl
oxide, methyl amyl ketone, cyclohexanone and other
aliphatic ketones; esters such as methyl acetate,
ethyl acetate, alkyl carboxylic esters; ethers, such
as methyl t-butyl ether, dibutyl ether, methyl phenyl
ether and other aliphatic or alkyl aromatic ethers;
glycol ethers such as ethoxy ethanol, butoxy ethanol,
ethoxy 2-propanol, propoxy ethanol, butoxy 2-propanol
and other glycol ethers; glycol ether esters such as
butoxy ethoxy acetate, ethyl 3-ethoxy propionate and
other glycol ether esters; alcohols such as methanol,
ethanol, propanol, iso-propanol, butanol,
iso-butanol, amyl alcohol and other aliphatic
alcohols; aromatic hydrocarbons such as toluene,
xylene, and other aromatics or mixtures of aromatic
solvents; aliphatic hydrocarbons such as VM&P naphtha
and mineral spirits, and other aliphatics or mixtures
of aliphatics; nitro alkanes such as 2-nitropropane.
A review of the structural relationships important to
the choice of solvent or solvent blend is given by
Dileep et al., Ind. Eng. Chem. (Product Research and
Development) 24, 162, 1985 and Francis, A. W., J.
Phys. Chem. 58, 1099, 1954.

Of course, there are solvents which can
function both as coupling solvents as well as active

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solvents and the one solvent may be used to
accomplish both purposes. Such solvents include, for
example, butoxy ethanol, propoxy ethanol and propoxy
2-propanol. Glycol ethers are particularly preferred.

    Suitable additives that are conventionally
present in coating formulations that are intended for
spray application may also be present in this
invention, such as, curing agents, plasticizers,
surfactants, and the like.

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Examples of compounds which may be used as the subcritical compressed fluids are given in Table 1.

TABLE 1

EXAMPLES OF SUBCRITICAL COMPRESSED FLUIDS

Compound	Boiling Point (C)	Critical Temperature (C)	Critical Pressure (atm)	Critical Density (g/ml)
Carbon Dioxide	-78.5	31.3	72.9	0.448
Nitrous Oxide	-88.56	36.5	71.7	0.45
Ammonia	-33.35	132.4	112.5	0.235
Xenon	-108.2	16.6	57.6	0.118
Ethane	-88.63	32.28	48.1	0.203
Propane	-42.1	96.67	41.9	0.217
Chlorotrifluoro-methane	-31.2	28.0	38.7	0.579
Monofluoromethane	-78.4	44.6	58.0	0.3

Preferably, the subcritical compressed fluid has a critical temperature above the ambient temperature of the spray environment and has appreciable solubility in the coating composition.

Moreover, the subcritical compressed fluid is preferably environmentally compatible, can be made environmentally compatible by treatment, or can be readily recovered from the spray environment. For example, carbon dioxide is environmentally compatible. Nitrous oxide can be made

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environmentally compatible by natural decomposition
in the environment, or by heating to thermally
decompose it, to form molecular nitrogen and oxygen.
Ethane and propane can be made environmentally
compatible by incineration to carbon dioxide and
water. Ammonia is highly soluble in water and can be
removed and recovered from air streams by absorption
methods such as an air/water scrubber. Other methods
can also be used such as adsorption.

The utility of any of the above-mentioned
compounds as subcritical compressed fluids and
viscosity reducing diluents in the practice of the
present invention will depend upon the polymeric
compound(s) and the specific solvent fraction used
taking into account the temperature and pressure of
application and the inertness of the subcritical
compressed fluid with the remaining constituents of
the coating composition.

Due to their environmental compatibility,
low toxicity, non-flammability, favorable physical
properties at ambient temperature, and high
solubility in coating compositions, subcritical
compressed carbon dioxide and nitrous oxide are
preferably used in the practice of the present
invention. Due to its low cost and wide
availability, subcritical compressed carbon dioxide
is most preferred. However, use of any of the
aforementioned compounds and mixtures thereof are to
be considered within the scope of the present
invention. For example, mixtures of subcritical

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compressed carbon dioxide and nitrous oxide may be
useful because nitrous oxide is more polar than
carbon dioxide and has different solvent properties.
Subcritical compressed ammonia has still higher
polarity and even relatively small amounts in
combination with subcritical nitrous oxide may be
useful to obtain higher solubility in some coating
compositions. Subcritical compressed ammonia tends
to react with subcritical compressed carbon dioxide,
but this may be useful with some coating compositions.

One of the more important discoveries made
during the development of processes for the spray
application of coatings using supercritical fluids
was that supercritical fluids not only function as a
viscosity reducer, but that they can also produce
vigorous decompressive atomization by a new airless
spray atomization mechanism. This greatly improves
the airless spray process so that high quality
coatings can be applied. We have discovered that
subcritical compressed fluids also can produce such
decompressive atomization as well.

Airless spray techniques use a high pressure
drop across the spray orifice to propel the coating
formulation through the orifice at high velocity.
The conventional atomization mechanism is well known
and is discussed and illustrated by Dombroski, N. and
Johns, W. R., Chemical Engineering Science 18: 203,
1963. The coating exits the orifice as a liquid film
that becomes unstable from shear induced by its high
velocity relative to the surrounding air. Waves grow

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in the liquid film, become unstable, and break up
into liquid filaments that likewise become unstable
and break up into droplets. Atomization occurs
because cohesion and surface tension forces, which
hold the liquid together, are overcome by shear and
fluid inertia forces, which break it apart. As used
herein, "liquid-film atomization" and "liquid-film
spray" refers to a spray, spray fan, or spray pattern
in which atomization occurs by this conventional
mechanism from a visible liquid film that extends
wholly or partly from the spray orifice. In
liquid-film atomization, however, the cohesion and
surface tension forces are not entirely overcome and
they profoundly affect the spray, particularly for
viscous coating formulations. Conventional airless
spray techniques are known to produce coarse droplets
and defective spray fans that limit their usefulness
to applying low-quality coating films. Higher
viscosity increases the viscous losses that occur
within the spray orifice, which lessens the energy
available for atomization, and it decreases shear
intensity, which hinders the development of natural
instabilities in the expanding liquid film. This
delays atomization so that large droplets are
formed. The spray also characteristically forms a
"tailing" or "fishtail" spray pattern (discussed
later), which makes it difficult to apply a uniform
coating.

In the spray application of coatings using
supercritical fluids, the large concentration of
dissolved supercritical fluid produces a liquid spray

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mixture with markedly different properties from
conventional coating compositions. In particular,
the mixture of coating composition and supercritical
fluid produces a liquid spray mixture that is highly
compressible, that is, the density changes markedly
with changes in pressure, whereas conventional
coating compositions are incompressible liquids when
they are sprayed. Without wishing to be bound by
theory, it is believed that vigorous decompressive
atomization can be produced by the dissolved
supercritical fluid such as supercritical carbon
dioxide suddenly becoming exceedingly supersaturated
as the spray mixture leaves the nozzle and
experiences a sudden and large drop in pressure.
This creates a very large driving force for
gasification of the carbon dioxide, which overwhelms
the cohesion, surface tension, and viscous forces
that oppose atomization and normally bind the fluid
flow together into a fishtail type of spray. A
different atomization mechanism is evident because
atomization occurs right at the spray orifice instead
of away from it as is conventional. Atomization is
believed to be due not to break-up of a liquid film
from shear with the surrounding air but instead to
the expansive forces of the compressible spray
solution created by the large concentration of
dissolved supercritical fluid. Therefore, no liquid
film is visible coming out of the nozzle.
Furthermore, because the spray is no longer bound by
cohesion and surface tension forces, it leaves the
nozzle at a much wider angle than normal airless
sprays and produces a "feathered" spray (discussed
later) with tapered edges like an air spray. This

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produces a rounded parabolic-shaped spray fan instead
of the sharp angular fans typical of conventional
airless sprays. The spray also typically has a much
wider fan width than conventional airless sprays
produced by the same spray tip. As used herein,
"decompressive atomization" and "decompressive spray"
refers to a spray, spray fan, or spray pattern that
has the preceding characteristics and in which no
liquid film in whole or in part is visible extending
from the spray orifice. Laser light scattering
measurements and comparative spray tests show that
this decompressive atomization can produce fine
droplets that are in the same size range as air spray
systems (20 to 50 microns) instead of the coarse
droplets produced by normal airless sprays (70 to 150
microns). For a properly formulated coating
composition, the droplet size range and distribution
are ideal for minimizing orange peel and other
surface defects commonly associated with spray
application. This fine particle size provides ample
surface area for the dissolved supercritical fluid to
very rapidly diffuse from the droplets within a short
distance from the spray nozzle. Therefore, the
coating is essentially free of the supercritical
fluid before it is deposited onto the substrate.

Experience with the spray application of
coating compositions using supercritical fluids and
known differences between supercritical and
subcritical fluids provided many reasons for one
skilled in the art to believe that using subcritical
fluids as viscosity reducers to spray apply coating

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compositions would not be possible and would not be
an effective method of reducing organic solvent usage:

Firstly, it was believed that sufficient
viscosity reduction to obtain the required low spray
viscosity would not be possible for several reasons.
Conventional coating compositions have a very low
spray application viscosity. Even conventional
high-solids coatings have a low spray application
viscosity, typically 80 centipoise for clear coats
and 35 centipoise for base coats. But coating
compositions applied by using supercritical fluids
have very high viscosities, typically ranging from
500 to 3000 centipoise, because much if not most of
the organic solvent has been eliminated and replaced
by the supercritical fluid to obtain viscosity
reduction for spraying. To be effective at
eliminating organic solvents, coating compositions
sprayed with subcritical fluids would have the same
high viscosities. But in the heated sprays typically
used with supercritical fluids, some of the viscosity
reduction is due to the increased temperature. For
example, an acrylic coating composition that has a
viscosity of 1000 centipoise at the ambient
temperature of 25 C has a viscosity of 300 centipoise
when heated to a spray temperature of 50 C. Adding
supercritical carbon dioxide to a concentration of
28% by weight, which is near the solubility limit,
reduces the viscosity to 30 centipoise for spraying.
Therefore, whereas the supercritical carbon dioxide
need only reduce the viscosity from 300 to 30 ·
centipoise, subcritical carbon dioxide at the ambient

temperature would have to reduce the viscosity from 1000 to 30 centipoise for spraying, a three-fold larger reduction. The reduction in viscosity that occurs from heating the coating composition is lost at subcritical temperatures. Furthermore, because of the lower, subcritical pressure, subcritical carbon dioxide would be expected to have lower solubility by one skilled in the art; therefore the higher solubility that would be needed to obtain the much greater reduction in viscosity would not be possible. This would necessitate using much more organic solvent to obtain a low spray viscosity, which is contrary to the need to significantly reduce organic solvent usage.

Secondly, one of the main reasons that supercritical fluids are used in some applications instead of subcritical fluids is the well known fact that supercritical fluids are highly compressible. Therefore, it would be believed by those skilled in the art that using much less compressible subcritical fluids as a viscosity reducer would produce a spray mixture with much less compressibility. This would be compounded by the lower solubility at lower pressure. In addition, the lower subcritical spray temperature would significantly reduce the degree of supersaturation achieved when the spray mixture is sprayed, which reduces the driving force for gasification of the subcritical fluid. Hence, those skilled in the art would believe that the decompressive expansive force would be insufficient to obtain the vigorous atomization needed for fine

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droplet size and high quality coatings. Poor
atomization with large droplets would significantly
increase the time required for the subcritical fluid
to diffuse and escape from solution in the droplets.
This would be compounded by lower diffusivity at
lower temperature. Therefore, a coating would be
deposited that was foamy or full of bubbles formed
from the subcritical fluid that remained dissolved in
the coating composition.

Thirdly, when supercritical fluids are used,
the spray mixture can be heated to a temperature that
counteracts the large cooling effect caused by rapid
expansion of the supercritical fluid as free gas from
the spray. This is necessary to keep the spray from
cooling significantly to below ambient temperature.
Typically, this requires a temperature of from about
50 to 60 C. However, when spraying at ambient or
near ambient temperatures, the large cooling effect
is not counteracted and the spray would therefore
cool quickly to a very low temperature. This is
undesirable because it could cause moisture
condensation and would deposit very cold and very
viscous droplets on the substrate that would be
unable to coalesce and flow to form a smooth coherent
high quality coating.

The first spray experiments we made using
subcritical fluids as viscosity reducing diluents
appeared to confirm these expectations. Numerous
attempts to spray apply several different coating
compositions, which were successfully sprayed using

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supercritical carbon dioxide at high temperature
(50-60 C) and high pressure (1500-1700 psi), by using
subcritical carbon dioxide at ambient temperatures
and low pressures (800-1000 psi) failed to produce
useable sprays and useable coatings. In fact, the
coatings were worse with subcritical carbon dioxide
than if the viscous coating compositions were sprayed
as is with no subcritical carbon dioxide added as a
viscosity reducer. These attempts all resulted in
fishtail liquid-film sprays being produced, and
decompressive atomization was not obtained. These
sprays deposited a thick layer of foam on the
substrate when a thin coherent bubble-free smooth
coating was desired. The measured temperature
profile of the spray produced using an acrylic
coating composition with an ambient viscosity of 1000
centipoise (discussed earlier) is shown in Figure 8.
This showed that most of the subcritical carbon
dioxide had already diffused from the liquid film
before atomization occurred about one-half inch from
the orifice. The liquid film was rapidly cooled by
this loss of dissolved carbon dioxide to a
temperature that was 36 degrees C below ambient
temperature. Therefore, atomization occurred under
very unfavorable conditions. Not only was there
little viscosity reduction by the subcritical carbon
dioxide, which had already diffused from the liquid
film, but the liquid film was at a very low
temperature, which substantially increased the
viscosity of the coating composition. Therefore,
instead of reducing the viscosity to a very low
level, the subcritical carbon dioxide increased the

viscosity to a higher level when atomization
occured. This produced very poor atomization and
large droplet sizes that were too large and too cold
for the remaining carbon dioxide to diffuse from the
droplets. This remaining carbon dioxide produced a
layer of foam instead of a smooth coating on the
substrate. Furthermore, the large droplets had too
much thermal mass to be warmed appreciably by
entrainment of surrounding ambient air into the
spray. The layer of foam was deposited with a
temperature that was twelve degrees C below ambient
temperature. Therefore, the deposited coating
composition was much more viscous than if it had been
deposited at ambient temperature, which hindered
coalescence and flow out of the coating. Adding
organic solvent to decrease the viscosity of the
coating composition did not change the very poor
liquid-film spray into an improved decompressive
spray as was desired. Instead, the layer of foam more
readily ran off of the substrate.

        In contrast, Figure 8 shows the measured
temperature profile for the same coating composition
sprayed with the same concentration of supercritical
carbon dioxide as the viscosity reducer, with the
spray mixture heated to 60 C to offset the cooling
effect of the carbon dioxide escaping from the
spray. This produced a spray that cooled to ambient
temperature within one inch of the orifice, without
subcooling below ambient temperature. The
decompressive spray produced a thin coherent
bubble-free high quality coating as desired.

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It was not until after further spray
attempts were made that we discovered that
subcritical fluids such as subcritical carbon dioxide
can be successfully used as viscosity reducers and
atomization enhancers to apply high quality coatings
provided the coating composition has favorable
properties. In particular, it was discovered that it
is necessary that the coating composition (1)
contains primarily polymer components that have a
sufficiently low number-average molecular weight and
(2) contains a relatively low amount of polymer
components that have high weight-average molecular
weight. Other properties were also discovered to be
desirably present, as will be discussed later.

Without wishing to be bound by theory, it is
believed that the primary requirement for spraying
coating compositions with subcritical fluids is that
the spray mixture formed must have sufficiently low
cohesiveness and related properties such as
elasticity, viscosity, and surface tension, all of
which serve to bind the liquid spray mixture together
and which oppose atomization, to compensate for the
reduced compressibility and reduced supersaturation
driving force for gasification that results from
using a subcritical fluid instead of a supercritical
fluid as the viscosity reducer. That is, the
cohesion, elastic, surface tension, and viscosity
forces in the composition should desirably be
sufficiently low to be overcome by the reduced
expansive force of the subcritical fluid in order to

produce vigorous atomization that produces high
quality coatings.

Vigorous decompressive atomization is
preferred, but we have also discovered that vigorous
liquid-film atomization can occur and produce
acceptable coatings with subcritical fluids as
viscosity reducers if the coating composition
contains sufficiently low molecular weight polymers
and preferably has sufficiently low viscosity.
Without wishing to be bound by theory, it is believed
that acceptable liquid-film atomization can occur
with subcritical fluids in situations where the
reduced expansive force is insufficient to produce
decompressive atomization but the driving force for
gasification of the subcritical fluid produces great
instability in the liquid film, so that atomization
occurs within a relatively short distance from the
spray orifice. This would occur before a significant
amount of subcritical fluid is lost from the liquid
film and before significant cooling occurs. Although
this is believed to produce larger droplet size than
in decompressive atomization, a lower viscosity
coating composition is able to compensate for this by
more readily venting the subcritical fluid from the
spray droplets and from the deposited coating.

High molecular weight polymers are
undesirable for atomization because the higher the
molecular weight of the polymer, the longer the
polymer chains are. Therefore, each individual
polymer chain is able to interact with a much greater

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number of other chains by such physical means as
chain entanglement or such chemical means as hydrogen
bonding or other associations between consitituent
groups on the polymer chain. Furthermore, long
polymer chains are able to more readily interact with
themselves and form configurations that make the
chain more rigid and less able to yield under
stress. These interactions lead to an extended
network of associated chains that greatly increases
the cohesiveness of the spray mixture. These
interactions also greatly increase viscosity, so that
stresses are readily dissipated and do not propagate
far. Long polymer chains also create elastic forces,
that is, restorative forces that act like springs to
return the polymer chain and thereby the extended
network to its original conformation after stress is
reduced. The high expansive force of supercritical
fluids is able to overcome these opposing forces but
the weaker expansive force of subcritical fluids is
less able to do so.

        In contrast, low molecular weight polymers
are more desirable for atomization because they have
short polymer chains. Hence, each chain interacts
with just a small number of other chains. The
network of associated chains is localized and easily
disrupted. The chains interact less with themselves
and are therefore more flexible. Viscosity is
relatively low, so stresses do not dissipate and they
propagate farther. Elastic forces are weak or
absent. Therefore, the weaker expansive force of
subcritical fluids is better able to overcome these

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weaker opposing forces and produce vigorous
atomization.

Polymers typically have a distribution of
molecular weights, which are generally characterized
by two measures: the number-average molecular weight
and the weight-average molecular weight. Letting W_i
be the weight fraction "i" in the distribution with
molecular weight M_i, the number-average molecular
weight M_n can be calculated from the formula:

$$M_n = [Sum_i \ W_i]/[Sum_i \ (W_i/M_i)]$$
$$= 1/[Sum_i \ (W_i/M_i)] \qquad (I)$$

and the weight-average molecular weight M_w can be
calculated from the formula:

$$M_w = [Sum_i \ W_iM_i]/[Sum_i \ W_i]$$
$$= Sum_i \ W_iM_i \qquad (II)$$

where the summations are over all weight fractions
"i" in the distribution. The number-average
molecular weight M_n is influenced more by the
low-molecular-weight end of the distribution and the
weight-average molecular weight M_w is influenced more
by the high-molecular-weight end of the
distribution. Therefore, the ratio M_w/M_n is a
measure of the span of the distribution.

We have discovered that the number-average
molecular weight correlates better with good

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sprayability than does the weight-average molecular
weight for coating compositions that consist mainly
of low molecular weight polymers. Low molecular
weight polymers have short polymer chains, so end
groups are much more important in forming
associations between chains than in high molecular
weight polymers and affect cohesiveness more. The
small polymer chains in the distribution also
separate the long chains and minimize their
entanglement and interactions, that is, the small
chains reduce network formation. This is better
reflected by the number-average molecular weight than
by the weight-average molecular weight of the polymer.

It has also been discovered that the
molecular weight of the polymer affects the
solubility of supercritical fluids such as
supercritical carbon dioxide, and we believe that
this effect is also applicable to subcritical fluids
as well. With all other factors remaining constant,
measurements show that carbon dioxide solubility
decreases relatively rapidly with increasing
molecular weight up to a weight-average molecular
weight of about 15,000, and then decreases much more
slowly. This indicates that carbon dioxide interacts
more with low molecular weight polymers than with
high molecular weight polymers, that is, when there
is a relatively high concentration of polymer end
groups. This suggests that carbon dioxide interacts
with and hence solvates end groups better than the
internal chain segments of the polymer. Therefore,

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carbon dioxide is more effective at preventing
interactions between end groups and hence for
disrupting the cohesiveness of the polymer network
when the polymer has low molecular weight. This
effect is also reflected better by the number-average
molecular weight.

In particular, we have discovered that
subcritical compressed fluids can be utilized as
viscosity reducing diluents when the coating
composition contains one or more polymeric compounds
that have a number-average molecular weight that is
less than about 5,000. Preferably, the
number-average molecular weight is less than about
3,500. Most preferably, the number-average molecular
weight is less than about 2,500.

We have also discovered that subcritical
compressed fluids can be utilized as viscosity
reducing diluents when the coating composition
contains an additional one or more polymeric
compounds that have higher number-average molecular
weights than those noted above provided that at least
75 weight percent of the total weight of all
polymeric compounds in the composition has a
weight-average molecular weight of less than about
20,000. Preferably, at least 80 percent of the total
weight of all polymeric compounds has a
weight-average molecular weight less than about
15,000. Most preferably, at least 85 percent of the
total weight of all polymeric compounds has a
weight-average molecular weight of less than about

10,000. If the high-molecular-weight polymer
compounds are sufficiently diluted by the
low-molecular-weight polymer compounds, then extended
networks are not effectively formed and do not
increase cohesiveness detrimentally to atomization.

In order to provide an effective coating
composition, the weight-average molecular weight of
all the polymeric compounds when taken as a whole
should be greater than 500. Preferably the
weight-average molecular weight of all the polymeric
compounds when taken as a whole should be greater
than 1,000. Most preferably, the weight-average
molecular weight of all the polymeric compounds when
taken as a whole should be greater than 2,000.

Due to the low molecular weights of the
polymer compounds, polymer systems are preferred that
can be cross-linked or otherwise reacted to increase
the molecular weight of the polymers after deposition
in order to provide a hard coating. This includes
polymer systems that are cured by heating, by using
catalysts, or air dry systems that react with oxygen
or react after solvent loss. Polymer systems that
are used in conventional high-solids coatings and
polymer systems that utilize low molecular weight
cross-linking agents are also preferred. Preferred
polymers are acrylics, polyesters, melamines, alkyds,
epoxies, urethanes, urea formaldehydes, and vinyls
and mixtures thereof. Most preferred are polymer
systems having high solubility for the subcritical
fluid. For mold release applications, silicone

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polymers are preferred, such as polydimethylsiloxane
and related silicone polymers.

The use of liquid polymers having the
desired molecular weight, that is, polymers which are
in the liquid state at ambient temperature and
pressure conditions, are also within the scope of the
present invention and indeed are preferred. By
combining a subcritical compressed fluid with the
liquid polymer(s), the viscosity of the resulting
liquid mixture is reduced to the point where it is
easily transportable, such as by being sprayed. In
this manner, no other solvent, such as an active
solvent, is required thereby totally eliminating
volatile organic solvents from the system.

In addition to the molecular weight of the
one or more polymeric components contained in the
composition being an important parameter for
obtaining the desired viscosity reducing diluent
effect when utilizing a subcritical compressed fluid
such that the composition may be sprayed, if so
desired, it is also preferable that the solubility of
the composition with the subcritical compressed fluid
as well as its viscosity also be considered.

Accordingly, it is also desirable that the
composition, such as a coating composition, have
solubility characteristics which maximize the
viscosity reducing effect of the subcritical
compressed fluid and if the admixed coating
composition is to be sprayed, solubility

characteristics which provide for a desirable
coating. Thus, the solubility of the subcritical
compressed fluid with the composition in its
subcritical compressed state and, if sprayed, at the
conditions of the substrate should desirably be
optimized.

The solubility requirements for these two
sets of conditions are totally antithetical to one
another. Thus, when admixing the subcritical
compressed fluid with the coating composition, it is
desirable to have a composition which has a high
solubility for the subcritical compressed fluid. In
contrast, once the admixed coating composition is
sprayed, for example, it is desirable that the
solubility for the fluid at the conditions present in
the environment of the substrate be as low as
possible.

Accordingly, it is preferable that the
composition containing the one or more polymeric
compounds have an overall solubility with the
subcritical compressed fluid at the temperature and
pressure of admixture with the composition (prior to
spraying) of at least 10% by weight of the
subcritical compressed fluid in the liquid mixture
that is formed. Preferably, the solubility should be
at least about 15% by weight of the subcritical
compressed fluid in the mixture, and more preferably,
about 20 to 70% or greater by weight on the same
basis. Most preferably, it is in the range of from
about 25% to about 50% by weight.

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Figure 9 illustrates how carbon dioxide solubility increases with pressure at two temperatures that are representative of spraying with subcritical compressed carbon dioxide (25 C) and with supercritical carbon dioxide (60 C). The coating composition contains an acrylic polymer (Acryloid[tm] AT-954) and a melamine cross-linking agent (Cymel[tm] 323) that have low number-average molecular weights of 1,670 and 410, respectively. The coating composition has a high total polymer content of 75%. At the supercritical temperature of 60 C, the solubility increases relatively linearly with pressure, but at the subcritical temperature of 25 C, the solubility is higher and, surprisingly, markedly increases between pressures of 700 and 900 psi and then levels off at a higher level than at 60 C. This would appear to indicate that subcritical carbon dioxide interacts more strongly with the polymer than supercritical carbon dioxide does, which increases the solubility to a level at relatively low pressures that is favorable for viscosity reduction and for obtaining vigorous decompressive atomization. The viscosity reduction that results is shown in Figure 10 as a function of the concentration of dissolved subcritical carbon dioxide.

If the composition is only to be made transportable, then the solubility aspect with the subcritical compressed fluid is all that needs to be considered. However, if the composition is to be sprayed, then it is desirable to have the subcritical

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compressed fluid diffuse through the sprayed
composition as quickly as possible such that there is
very little residual fluid left in the coating once
it has come into contact with the substrate.
Accordingly, the fluid, which of course is no longer
compressed (at least to the extent that it was prior
to spraying), should have a solubility with the
coating composition of less than about 0.8% by weight
of the fluid in the non-compressed state in the
composition. Preferably, the solubility of the fluid
is less than about 0.6% by weight in the
composition. Most preferably, the fluid should be
soluble in the coating composition in an amount of
less than about 0.4%. As used herein, it is to be
understood that the solubility of the fluid in the
non-compressed state, i.e., at one atmosphere
pressure, is measured at 25°C and at one atmosphere
absolute pressure of the fluid.

If the composition is intended to be
sprayed, then the starting viscosity should desirably
also be considered. It should have a viscosity of
less than about 4,000 centipoise, and preferably less
than about 2,000 centipoise, and most preferably in
the range of from about 500 to about 1,500
centipoise. Obviously, a major factor contributing
to the viscosity of the liquid mixture is the amount
of solvent fraction contained therein. Hence, it is
apparent that the amount of solvent fraction present
in the composition should be considered hand-in-hand
with the desired viscosity that is to be obtained.

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The viscosity of the coating composition should be low enough such that there is enough solvent present to provide proper coalescence upon the substrate once the composition is sprayed while still being high enough to allow for a reduction in solvent usage so as to maximize the utilization of the subcritical compressed fluid viscosity diluent and to concomitantly facilitate good atomization and coating formation.

The viscosity of the coating composition should also be such that when subcritical compressed fluid is added, it is possible to add enough of the subcritical compressed fluid such that the viscosity is lowered to less than about 150 centipoise at the conditions of the subcritical compressed fluid so as to render the liquid mixture suitable for spray application. More preferably, the admixed coating composition has a viscosity which is less than about 100 centipoise and preferably has a viscosity of from about 1 to about 75 centipoise. Most preferably, the viscosity of the admixture of solids fraction, solvent fraction and subcritical compressed fluid is in the range of from about 5 to about 50 centipoise.

If the composition is not meant to be sprayed, but rather, transported by some other means such as by pumping, and the like, then the subcritical compressed fluid should be present in quantities such that a liquid mixture is formed which possesses a viscosity such that it is readily transportable by whatever means is desired.

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Where a solvent fraction is utilized, the
polymeric component of the liquid mixture is
generally present in amounts ranging from 10 to 75
weight percent based upon the total weight of the
polymer(s), solvent fraction, and subcritical
compressed fluid. Preferably, the polymer component
is present in amounts ranging from about 20 to about
65 weight percent on the same basis.

If subcritical compressed carbon dioxide
fluid is utilized as the subcritical viscosity
reducing diluent, it preferably should be present in
amounts ranging from about 10 to about 75 weight
percent based upon the total weight of the
polymer(s), solvent fraction and subcritical fluid.
Most preferably, it is present in amounts ranging
from 20 to 60 weight percent on the same basis
producing a liquid mixture having a viscosity in the
range of from about 5 centipoise to about 50
centipoise.

In order to minimize the unnecessary release
of any active solvent present in the liquid spray
mixture, the amount of active solvent used should be
less than that required to produce a mixture of
polymeric compounds and active solvent having a
viscosity which will permit its application by liquid
spray techniques. In other words, the inclusion of
active solvent(s) should be minimized such that the
viscosity diluent effect provided by the subcritical
compressed fluid in accordance with the present

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invention is fully utilized. Generally, this
requires that the mixture of polymeric compounds and
active solvent have a viscosity of not less than
about 150 centipoise. Preferably, the solvent(s)
should be present in amounts ranging from about 0 to
about 70 weight percent based upon the total weight
of the polymer(s), solvent(s) and subcritical fluid.
Most preferably, the solvent(s) are present in
amounts ranging from about 5 to about 50 weight
percent on the same basis.

Generally, the temperature and pressure of
the subcritical compressed fluid used as the
viscosity reducing diluent and atomization enhancer
with the coating composition is as low as possible
while still obtaining the desired viscosity reducing
effect and desired atomization and spray
characteristics. Generally, temperatures are
preferred at which the subcritical compressed fluid
has a ratio of gas density to liquid density at
equilibrium of greater than about 0.1 regardless of
the pressure that is utilized. If the pressure is
greater than the critical pressure of the subcritical
compressed fluid, then it is desirable that the
temperatures be such that the ratio of gas density to
liquid density at equilibrium be less than about
0.8. Alternatively, if the pressure is less than
the critical pressure of the subcritical compressed
fluid, then the temperatures should desireably be
less than about 20 degrees C above the critical
temperature of the subcritical compressed fluid.

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More preferably, temperatures are utilized
at which the subcritical compressed fluid has a ratio
of gas density to liquid density at equilibrium of
greater than about 0.25 regardless of the pressure
that is utilized. If the pressure is greater than
the critical pressure of the subcritical compressed
fluid, then it is desirable that the temperatures be
such that the ratio of gas density to liquid density
at equilibrium be less than about 0.6.
Alternatively, if the pressure is less than the
critical pressure of the subcritical compressed
fluid, then the temperatures should desireably be
less than about 10 degrees C above the critical
temperature of the subcritical compressed fluid. At
these temperatures the subcritical compressed fluid
has high compressibility in both the liquid and gas
phases. Of course, the less energy used to either
heat or cool the fluid the better. Most preferably,
the temperature at which the subcritical compressed
fluid is used as the viscosity reducing diluent and
atomization enhancer is at ambient or near ambient
temperature. Cooling the fluid is generally not
beneficial for it typically tends to increase the
viscosity of the admixed composition. Excessive
heating of the fluid is also unnecessary and it is
one of the objectives of the present invention to
avoid such excessive heating so as to prevent
possible thermal degradation of the composition
constituents.

The pressure at which the subcritical
compressed gas is provided is as low as possible and

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is able to provide the viscosity reducing effect desired at the temperature and pressure chosen. This is typically dependent upon the composition that is to be admixed with the subcritical compressed fluid and the amount of active solvent that it contains.

When the composition is to be sprayed, the pressure of the subcritical compressed fluid will be that of the spray pressure. This spray pressure too is a function of the coating composition, the subcritical compressed fluid being used, and the viscosity of the liquid mixture formed by admixing the subcritical compressed fluid and the coating composition. The minimum spray pressure must be at least about 300 psi greater than the environment into which the composition will be sprayed, typically into atmospheric or near atmospheric pressure. Generally, the pressure will be less than about 95 percent of the absolute critical pressure of the subcritical compressed fluid if the temperature is above the critical temperature of such subcritical compressed fluid. The pressure will be less than about 600 psi above the absolute critical pressure of the subcritical compressed fluid if the temperature is below the critical temperature of such subcritical compressed fluid. Preferably, the spray pressure is in the range of from about 50 percent to about 90 percent of the absolute critical pressure of the subcritical compressed fluid. If the subcritical compressed fluid is subcritical compressed carbon dioxide fluid, the preferred spray pressure is between about 500 psia and about 1020 psia. The most

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preferred spray pressure is between about 700 psia
and about 970 psia.

     If the composition is to be sprayed, the
spray temperature used is a function of the coating
composition, the subcritical compressed fluid being
used, and the concentration of subcritical compressed
fluid in the liquid mixture. As the temperature is
decreased, the viscosity of the admixed composition
generally tends to increase. Accordingly, the
minimum spray temperature is that temperature at
which the admixed coating composition would have a
maximum viscosity needed for obtaining desirable
spray characteristics which was discussed earlier.
The maximum temperature is the highest temperature at
which the components of the liquid mixture are not
significantly thermally degraded during the time that
the liquid mixture is at that temperature. However,
it is most preferred that the temperature be the same
or nearly the same temperature at which the substrate
is maintained, generally ambient temperature.

     The subcritical compressed fluid maintained
at a given temperature and pressure may be mixed with
a composition which is at a different temperature and
pressure. The resulting temperature and pressure of
the mixture would then have to be adjusted, if
necessary, to provide the desired conditions so as to
obtain the viscosity reducing effect of the fluid.
Thus, if a subcritical compressed fluid maintained at
a temperature of 20°C and a pressure 1000 psi were
introduced into a closed chamber containing a

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composition at a temperature of 0°C and 100 psi, and the resulting admixture produced a liquid mixture at 10°C and a pressure of 500 psi, it may be necessary to raise the pressure of the liquid mixture so as to obtain the desired viscosity reducing effect from the subcritical compressed fluid.

Alternatively, the material used as the subcritical compressed fluid may be introduced into the composition while still a gas at one set of temperature and pressure conditions, and then be heated and/or pressurized to the desired extent by heating the admixture and thereby provide the gas as a subcritical compressed fluid and its concomitant viscosity reducing effect.

The liquid mixture of polymers, the subcritical compressed fluid, and, optionally, an active solvent, may be sprayed onto a substrate to form a liquid coating thereon by passing the liquid mixture under pressure through an orifice into the environment of the substrate to form a liquid spray.

Coating compositions are commonly applied to a substrate by passing the coating composition under pressure through an orifice into air in order to form a liquid spray, which impacts the substrate and forms a liquid coating. In the coatings industry, three types of orifice sprays are commonly used; namely, air spray, airless spray, and air-assisted airless spray.

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Air spray uses compressed air to break up the liquid coating formulation into droplets and to propel the droplets to the substrate. The most common type of air nozzle mixes the coating formulation and high-velocity air outside of the nozzle to cause atomization. Auxiliary air streams are used to modify the shape of the spray. The coating formulation flows through the liquid orifice in the spray nozzle with relatively little pressure drop. Siphon or pressure feed, usually at pressures less than 18 psi, are used, depending upon the viscosity and quantity of coating formulation to be sprayed.

Airless spray, as discussed previously, uses a high pressure drop across the orifice to propel the coating formulation through the orifice at high velocity. Upon exiting the orifice, the high-velocity liquid breaks up into droplets and disperses into the air to form a liquid spray. Sufficient momentum remains after atomization to carry the droplets to the substrate. The spray tip is contoured to modify the shape of the liquid spray, which is usually a round or elliptical cone or a flat fan. Turbulence promoters are sometimes inserted into the spray nozzle to aid atomization. Spray pressures typically range from 300 to 5000 psi. The pressure required increases with fluid viscosity.

Air-assisted airless spray combines features of air spray and airless spray. It uses both compressed air and high pressure drop across the

orifice to atomize the coating formulation and to
shape the liquid spray, typically under milder
conditions than each type of atomization is generated
by itself.

Generally, the compressed air pressure and
the air flow rate are lower than for air spray.
Generally the liquid pressure drop is lower than for
airless spray, but higher than for air spray. Liquid
spray pressures typically range from 200 to 800 psi.
The pressure required increases with fluid viscosity.

Air spray, airless spray, and air-assisted
airless spray can also be used with the liquid
coating formulation heated or with the air heated or
with both heated. Heating reduces the viscosity of
the liquid coating formulation and aids atomization.

An orifice is a hole or an opening in a wall
or housing, such as in a spray tip of a spray nozzle
on a conventional or electrostatic spray gun through
which the liquid mixture flows in going from a region
of higher pressure, such as inside the spray gun,
into a region of lower pressure, such as a typical
air environment outside of the spray gun and around
the substrate. An orifice may also be a hole or an
opening in the wall of a pressurized vessel, such as
a tank or cylinder. An orifice may also be the open
end of a tube or pipe or conduit through which the
mixture is discharged. The open end of the tube or
pipe or conduit may be constricted or partially
blocked to reduce the open area.

Spray orifices, spray tips, spray nozzles, and spray guns used for conventional and electrostatic airless and air-assisted airless spraying of coating formulations such as paints. lacquers, enamels, and varnishes, are suitable for spraying the coating or adhesive compositions when admixed with subrcritical compressed fluids. Spray guns, nozzles, and tips are preferred that do not have excessive flow volume between the orifice and the valve that turns the spray on and off. Moreover, the spray guns, nozzles, and tips must be built to contain the spray pressure used.

There are a broad variety of spray devices that one may use in spraying the coating or adhesive compositions after it has been admixed with subrcritical compressed fluid. Essentially, any spray gun may be used containing essentially any nozzle tip, from conventional airless and air-assisted airless spray devices to electrostatic spray devices. The choice of spray device is dependent upon the kind of application that is contemplated.

The material of construction of the orifice through which the admixed liquid mixture is sprayed must possess the necessary mechanical strength for the high spray pressure used, have sufficient abrasion resistance to resist wear from fluid flow, and be inert to chemicals with which it comes into contact. Any of the materials used in the construction of airless spray-tips, such as boron

carbide, titanium carbide, ceramic, stainless steel
or brass, is suitable, with tungsten carbide
generally being preferred.

The orifice sizes suitable for spraying the
liquid mixture should generally range from about
.004-inch to about .072-inch diameter. Because the
orifices are generally not circular, the diameters
referred to are equivalent to a circular diameter.
The proper selection is determined by the orifice
size that will supply the desired amount of liquid
coating and accomplish proper atomization for the
coating. Generally, smaller orifices are desired at
lower viscosity and larger orifices are desired at
higher viscosity. Smaller orifices give finer
atomization but lower output. Larger orifices give
higher output but poorer atomization. Finer
atomization is preferred. Therefore, small orifice
sizes from about .004-inch to about .025-inch
diameter are preferred.

The designs of the spray tip that contains
the spray orifice and of the spray nozzle that
contains the spray tip are not critical. The spray
tips and spray nozzles should have no protuberances
near the orifice that would interfere with the
spray. The spray tips and nozzles should preferably
have minimal internal void space to produce a clean
shut off of the spray.

The shape of the spray is also not critical
to being able to spray the liquid mixture. The spray

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may be in the shape of a cone that is circular or
elliptical in cross section or the spray may be in
the shape of a flat fan, but the spray is not limited
to these shapes. Sprays that are flat fans or cones
that are elliptical in cross section are preferred.
The distance from the orifice to the substrate is
generally at a distance of from about 4 inches to
about 24 inches.

Devices and flow designs that promote
turbulent or agitated flow in the liquid mixture
prior to passing the liquid mixture under pressure
through the orifice may also be used. Such
techniques include but are not limited to, the use of
pre-orifices, diffusers, turbulence plates,
restrictors, flow splitters/combiners, flow
impingers, screens, baffles, vanes, and other
inserts, devices, and flow networks that are used in
airless spray and air-assisted airless spray.

Filtering the liquid mixture prior to flow
through the orifice is desirable in order to remove
particulates that might plug the orifice. This can
be done using conventional high-pressure paint
filters. A filter may also be inserted at or in the
gun and a tip screen may be inserted at the spray tip
to prevent orifice plugging. The size of the flow
passages in the filter should be smaller than the
size of the orifice, preferably significantly smaller.

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Electrostatic forces may be used to increase the proportion of coating composition that is deposited onto a substrate from the spray. This is commonly referred to as increasing the transfer efficiency. This is done by using a high electrical voltage relative to the substrate to impart an electrical charge to the spray. This creates an electrical force of attraction between the spray droplets and the substrate which causes droplets that would otherwise miss the substrate to be deposited onto it. When the electrical force causes droplets to be deposited on the edges and backside of the substrate, this effect is commonly referred to as wrap around.

Preferably the substrate is grounded, but it may also be charged to the opposite sign as the spray. The substrate may be charged to the same sign as the spray, but at a lower voltage with respect to ground, but this is of less benefit, because this produces a weaker electrical force of attraction between the spray and the substrate than if the substrate were electrically grounded or charged to the opposite sign. Electrically grounding the substrate is the safest mode of operation. Preferably the spray is charged negative relative to electrical ground.

The method of charging the spray is not critical provided the charging method is effective. The coating formulation can be electrically charged by applying high electrical voltage relative to the

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substrate and electrical current (1) within the spray
gun, by direct contact with electrified walls or
internal electrodes before leaving the orifice; (2)
after the spray emerges from the orifice by
electrical discharge from external electrodes located
near the orifice and close to the spray; or (3) away
from the orifice, by passing the spray through or
between electrified grids or arrays of external
electrodes before the spray is deposited onto the
substrate.

The apparatus can be used with high
electrical voltage in the range of about 30 to about
150 kilovolts. Higher electrical voltages are
favored to impart higher electrical charge to the
spray to enhance attraction to the substrate, but the
voltage level must be safe for the type of charging
and spray gun used. For safety reasons, the voltage
of hand spray guns is usually restricted to less than
70 kilovolts and the equipment is designed to
automatically shut off the voltage when the current
exceeds a safe level. Generally for hand spray guns
the useful range of electrical current is between 20
and 200 microamperes and optimum results are obtained
with coating formulations that have very low
electrical conductivity, that is, very high
electrical resistance. For automatic spray guns that
are used remotely, higher voltages and electrical
currents can be safely used than for hand spray
guns. Therefore the voltage can exceed 70 kilovolts
up to 150 kilovolts and the current can exceed 200
microamperes.

These methods of electrostatic charging are known to those who are skilled in the art of electrostatic spraying.

For electrostatic spraying, the substrate is preferably an electrical conductor such as metal. But substrates that are not conductors or semiconductors can also be sprayed. Preferably they are pretreated to create an electrically conducting surface. For instance, the substrate can be immersed in a special solution to impart conductivity to the surface.

The method of generating the high electrical voltage and electrical current is not critical. Conventional high voltage electrical power supplies can be used. The power supply should have standard safety features that prevent current or voltage surges. The electrical power supply may be built into the spray guns Other charging methods may also be used.

Typically, the spray undergoes rapid cooling while it is close to the orifice, so the temperature drops rapidly to below ambient temperature. Entrainment of ambient air into the spray warms the spray to near ambient temperature before the spray reaches the substrate provided that the spray has fine droplet size as shown in Figure 8. The droplets are further warmed by absorbing heat from the substrate when they are deposited. This rapid

cooling of the spray may be beneficial because less
active solvent evaporates in the spray in comparison
to the amount of solvent lost in conventional heated
airless sprays. Therefore, a greater proportion of
the active solvent is retained in the coating
formulation to aid leveling of the coating on the
substrate.

Spray temperatures above ambient may be
obtained by mildly heating the liquid mixture before
it enters the spray gun, by heating the spray gun
itself, by circulating the heated liquid mixture to
or through the spray gun to maintain the spray
temperature, or by a combination of such methods.
Circulating the heated liquid mixture through the
spray gun is preferred to avoid heat loss and to
maintain the desired spray temperature, provided the
application does not use color change.

The environment into which the admixed
coating composition is sprayed is not critical.
However, the pressure therein must be less than that
required to maintain the subcritical compressed fluid
component of the liquid spray mixture in the
compressed state. Preferably, the admixed liquid
coating composition is sprayed in air under
conditions at or near atmospheric pressure. Other
gas environments can also be used, such as air with
reduced oxygen content or inert gases such as
nitrogen, carbon dioxide, helium, argon, xenon, or a
mixture. Oxygen or oxygen enriched air is not
desirable, because oxygen enhances the flammability
of organic components in the spray.

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Generally, liquid spray droplets are produced which generally have an average diameter of one micron or greater. These liquid droplets contain a portion of the solids, a portion of the solvent, and a portion of the subcritical compressed fluid. Preferably, these droplets have average diameters of from about 10 to about 1000 microns. More preferably, these droplets have average diameters of from about 15 to about 200 microns. Most preferably, these droplets have average diameters of from about 20 to about 100 microns. Small spray droplets are desirable to vent the supercritical fluid from the spray droplet before impacting the substrate. Small spray droplets also give higher quality finishes.

The processes of the present invention may be used to apply coatings by the application of liquid spray to a variety of substrates. Examples of suitable substrates include, but are not limited to, metals, wood, glass, plastic, mold surfaces, paper, cloth, ceramic, masonry, stone, cement, asphalt, rubber, and composite materials, medicinal pills and tablets, and agriculturally related substrates.

Through the practice of the present invention, films may be applied to substrates such that the cured films have thicknesses of from about 0.2 to about 10.0 mils. Preferably, the films have thicknesses of from about 0.5 to about 8.0 mils, and most preferably, the thickness range is from about 0.8 to about 4.0 mils.

If curing of the coating composition present
upon the coated substrate is required, it may be
performed by conventional means, such as allowing for
evaporation of the active and/or coupling solvent,
application of heat or ultraviolet light, etc.

Compressed gas may be utilized to assist
formation of the liquid spray and/or to modify the
shape of the liquid spray that comes from the
orifice. The assist gas is typically compressed air
at pressures from 5 to 50 psi, but may also be air
with reduced oxygen content or inert gases such as
compressed nitrogen, carbon dioxide, helium, argon,
or xenon, or a mixture. Compressed oxygen or oxygen
enriched air is not desirable because oxygen enhances
the flammability of the organic components in the
spray. The assist gas is directed into the liquid
spray as one or more high-velocity jets of gas,
preferably arranged symmetrically on each side of the
liquid spray to balance each other. The assist gas
jets will preferably come from gas orifices built
into the spray tip and/or nozzle. The assist gas may
also issue from an opening in the spray tip or nozzle
that is a concentric annular ring that is around and
centered on the liquid orifice, to produce a
hollow-cone high-velocity jet of gas that converges
on the liquid spray, but this creates a larger flow
of assist gas that is not as desirable. The
concentric annular ring may be divided into segments,
to reduce gas flow rate, and it may be elliptical
instead of circular, to shape the spray.

Preferably, the flow rate and pressure of the assist
gas are lower than those used in air spray.
Preferably the assist gas is heated to counteract the
rapid cooling effect of the subcritical compressed
fluid diluent in the spray. The preferred
temperature of heated assist gas ranges from about
$35^{\circ}C$ to about $90^{\circ}C$.

We have also found that there are additives
that may be added to the liquid mixture which will
improve the atomization enhancement effect provided
by the subcritical fluid. For example, pigments and
other solid particulate additives such as fillers
have been found to expand the range of conditions in
which vigorous decompressive atomization can be
obtained. For example, a coating composition that
gives a clear coating that is difficult to atomize
can often give improved atomization by incorporating
pigment into the coating formulation. In particular,
titanium dioxide pigments have been found to give
better atomization at lower temperatures and also to
allow more subcritical compressed carbon dioxide to
be used in the spray mixture than would otherwise be
expected based on the coating formulation with no
pigment. Therefore, titanium dioxide is a preferred
pigment material.

Moreover, in commonly assigned U.S. Patent
Application Serial No. 599,792, filed October 16,
1990, the contents of which are incorporated herein
by reference as if set out in full, polymeric
compounds which provide an enhanced compatible

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relationship with supercritical or near-supercritical
fluids are disclosed. We have found that these
polymeric compounds are also applicable here and
provide such an enhancement effect with subcritical
fluids as well.

The thermoplastic or thermosettable
polymeric materials (that is, materials which at
their use temperatures are solids and typically solid
at normal room temperature, viz., 25°C.) that provide
this enhanced compatibility have, by virtue of
molecular disruptions along their backbone or pendant
to their backbone, a more open chain packing
conformation than more traditional polymer
compositions. This allows more subcritical fluid to
enter into solution with the polymer. As a result,
liquid mixtures are provided that have lower
viscosities and better transportability.

It has been determined that this enhanced
compatibility between subcritical fluid transporting
systems and organic polymeric compositions are
obtained by the inclusion in the polymeric
composition, of structural components which introduce
an expansive structure in the polymer. A common mode
of effecting an expansive polymeric structure is to
provide groups that expand the space required for
packing the polymeric molecules. This expands the
occupied volume of the polymer and thereby allows the
subcritical fluid to more effectively penetrate the
interstices between the polymer molecules. The
expansive structure may also comprise a function

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which destabilizes and blocks the formation of
coordination and associative structural relationships
along the polymer chain. It is the creation of this
expansivity, that achieves the greater compatibility
with the subcritical fluid, with the particular
polymers discussed in the 599,792 application.

As discussed therein, these polymers are
characterized by having a plurality of moieties with
the intermolecular disruption characteristics of
mono, di or tri substituted fluorine on carbon and
mono, di or tri substituted methyl on carbon or
silicon in which said carbon and silicon are directly
or indirectly covalently attached to the skeleton of
the polymer's main structure and is no more than
about 12 covalently bonded atoms from the covalent
linkage to an atom in the main structure of the
polymer. Preferred polymers include those containing
silicon and/or fluorine.

As noted above, conventional airless spray
techniques are known to produce defective spray fans
that limit their usefulness to applying low-quality
coating films. Characteristically, the liquid-film
spray forms a "tailing" or "fishtail" spray pattern,
which makes it difficult to apply a uniform coating.
By using subcritical compressed fluids, such as
subcritical compressed carbon dioxide, we have
discovered that an improved "feathered" airless spray
pattern can be formed which enables high-quality
uniform coatings to be applied, which is the
preferred embodiment of the present invention.

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Such proper atomization can easily be observed by the
shape and pattern of the spray that is produced
signifying that the proper spraying conditions are
being maintained as the coating mixture is sprayed.
In particular, as disclosed in related U.S. Patent
Application Serial No. 327,273, filed March 22, 1989,
a feathered spray pattern is clearly observed when
proper atomization of the coating mixture is being
obtained in contrast to a typical fishtail pattern.

The effect of spray conditions on a sprayed
coating mixture is vividly demonstrated in the
photoreproductions shown in Figures 5 to 8. In
Figures 6a - 6g, coating mixtures are sprayed either
with no subcritical compressed fluids or with
subcritical compressed fluids in too low a
concentration, for a given spray temperature and
pressure, such that various types of fishtail spray
patterns are formed. Surface tension and cohesive
forces in the liquid film tend to gather more liquid
at the edges of the spray fan than in the center,
which produces coarsely atomized jets of coating.
Sometimes the jets separate from the spray and
deposit separate bands of coating. At other times,
they thicken the edges so that more coating is
deposited at the top and bottom than in the center of
the spray. These deficiencies make it difficult to
apply a uniform coating. The fishtail spray pattern
characteristically forms when a liquid-film is
visible extending from the spray orifice before
atomization occurs. The fishtail sprays are also
generally angular in shape and have a relatively

narrow fan width, that is, a fan width that is not
much greater than the fan width rating of the spray
tip being used.

Figures 6a and 6b show fishtail spray
patterns produced by coating compositions containing
two high molecular weight polymers when sprayed with
no subcritical compressed fluid. Figure 6a was
produced by spraying an acrylic polymer (Acryloid^{TM}
B-66) having a high number-average molecular weight
of 24,750. The coating composition had a polymer
content of 44 percent and a viscosity of 1060
centipoise. The spray temperature was 27 C and the
pressure was 1,000 psi. The liquid-film is visible
extending a relatively long distance from the spray
orifice and the spray pattern consists primarily of
three jets of liquid at the edges and in the center
of the spray with little coating in between the
jets. Due to the high molecular weight, a feathered
spray pattern was not formed when subcritical
compressed carbon dioxide was utilized as the
viscosity reducing diluent, although a feathered
spray pattern was obtained using supercritical carbon
dioxide.

Figure 6b was produced by spraying cellulose
acetate butyrate polymer having a high number-average
molecular weight of 19,630. The coating composition
had a polymer content of 30 percent and a viscosity
of 1,290 centipoise. The spray temperature was 60 C
and the pressure was 400 psi. The liquid-film is
visible extending from the spray orifice and the

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spray pattern has a central portion and two detached
side jets with little coating in between. Due to the
high molecular weight, a feathered spray pattern was
not formed when subcritical compressed carbon dioxide
was utilized as the viscosity reducing diluent, even
though this polymer has very high carbon dioxide
solubility, although a feathered spray pattern was
obtained using supercritical carbon dioxide.

Figure 6c shows a fishtail spray pattern
produced by a coating composition containing
nitrocellulose polymer with a high number-average
molecular weight of 9,760 when sprayed with a
subcritical compressed carbon dioxide concentration
of about 30%. The coating composition had a
nitrocellulose content of 25.5% and a lower molecular
weight alkyd polymer content of 29.5%. The viscosity
was 500 centipoise. The spray temperature was 30.5 C
and the pressure was 1,000 psi. The liquid-film is
visible extending from the spray orifice and the
spray pattern has a higher concentration of coating
at the edges than in the center. The spray has a
narrow fan width and an angular shape. Due to the
high molecular weight, a feathered spray pattern was
not formed when subcritical compressed carbon dioxide
was utilized as the viscosity reducing diluent even
at much higher concentration, although a feathered
spray pattern was obtained using supercritical carbon
dioxide.

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Figures 6d - 6f show fishtail spray patterns produced by coating compositions containing a mixture of two acrylic polymers (Acryloid^{tm} AT-400 and AT-954) and a cross-linking agent (Cymel^{tm} 323) having low number-average molecular weights of 3,270, 1,670, and 410, respectively. In Figure 6d, a coating composition having a combined polymer content of 67% and a viscosity of 670 centipoise was sprayed without subcritical compressed fluid at a temperature of 28 C and a pressure of 1600 psi. The liquid film is visible and the spray pattern consists of a central portion with jets on each side. The spray has a narrow fan width and an angular shape.

Figure 6e shows the same coating composition diluted with 28% methyl ethyl ketone solvent to give a low viscosity to simulate addition of subcritical compressed carbon dioxide. The diluted polymer content was 48%. The spray temperature was 23 C and the pressure was 300 psi. Despite the much lower viscosity, the spray still has a fishtail pattern and a visible liquid film. The two side jets have detached farther from the central portion of the spray than in Figure 6d at high polymer concentration and higher viscosity.

In Figure 6f, the same coating composition as in Figure 6d is diluted with 28% subcritical compressed carbon dioxide to give a low viscosity. The spray temperature was 22 C and the spray pressure was 1,000 psi. The spray has a fishtail fan pattern with a visible liquid film and a greater

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concentration of coating at the edges of the spray
than in the center. The spray has a narrow fan width
and an angular shape. Increasing the subcritical
compressed carbon dioxide concentration to 31% and
decreasing the spray pressure to 850 psi desirably
produced a feathered spray fan, as shown in Figure 5a.

     Figure 6g shows a fishtail spray pattern
produced by a coating composition containing just a
single acrylic polymer (Acryloid^{tm} AT-954) having a
low number-average molecular weight of 1,670 and the
same cross-linking agent as in Figure 6d-6f. The
coating composition has a polymer content of 76% and
a viscosity of 1,100 centipoise. The spray mixture
had a subcritical compressed carbon dioxide
concentration of about 29%, a spray temperature of 24
C and a pressure of 1600 psi. The spray has a
visible liquid film and a greater concentration of
coating at the edges of the spray than in the
center. The spray has a narrow fan width and an
angular shape. Increasing the temperature to 27 C
and decreasing the pressure to 900 psi with the same
carbon dioxide concentration produced a wider
feathered spray fan with a uniform center and tapered
edges. The fan had a parabolic shape and no liquid
film was visible.

     In complete contrast to Figures 6a - 6g,
which are not in accordance with the preferred
embodiments of the present invention but still within
its scope, Figures 5a - 5f illustrate the preferred
feathered decompressive spray patterns of the present
invention obtained using a sufficient concentration

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of subcritical compressed carbon dioxide and proper
spray temperature and pressure. The sprays generally
have a parabolic shape, no visible liquid film, a
relatively uniform fan with tapered edges, and a
significantly greater fan width than the fan width
rating of the spray tip used. Figures 5a and 5b show
feathered decompressive sprays produced using the
same coating composition noted above in Figures 6d
and 6f. In Figure 5a, the subcritical compressed
carbon dioxide concentration is 31%, the spray
temperature is 21 C, and the pressure is 850 psi. In
Figure 5b, the subcritical compressed carbon dioxide
concentration is 30%, the spray temperature is 28 C,
and the pressure is 950 psi.

Figures 5c and 5d show feathered
decompressive sprays obtained using coating
compositions containing an acrylic polymer
(Acryloid^{tm} AT-400) with a number-average molecular
weight of 3,270 and the cross-linking agent noted
above. Figure 5c shows a clear coating composition
with a polymer content of 60% and a viscosity of 470
centipoise. The subcritical compressed carbon
dioxide content is 28%, the spray temperature is
36 C, and the spray pressure is 950 psi. Figure 5d
shows a white-pigmented coating composition with a
total solids content of 71% and a viscosity of 1200
centipoise. The subcritical compressed carbon
dioxide content is 32%, the spray temperature is
23 C, and the spray pressure is 900 psi.

Figures 5e and 5f show feathered
decompressive sprays obtained using coating
compositions containing an acrylic polymer
(Acryloid^{tm} AT-954) with a low number-average
molecular weight of 1,670 and the cross-linking agent
noted above. Figure 5e shows a clear coating
composition with a high polymer content of 79% and a
high viscosity of 3,000 centipoise. The subcritical
compressed carbon dioxide content is 28%, the spray
temperature is 28 C, and the spray pressure is 900
psi. Figure 5f shows a white-pigmented coating
composition with a high total solids content of 81%
and a viscosity of 540 centipoise. The subcritical
compressed carbon dioxide content is 39%, the spray
temperature is 24 C, and the spray pressure is 900
psi.

The characteristics of the coating
deposition profile which is obtained by spraying a
fishtail pattern of the type illustrated in Figures
6c and 6f onto a substrate is demonstrated in Figure
4. In Figure 4, a diagrammatic representation of the
coating particles is shown in which the edges of the
spray pattern contain a higher concentration of the
particles than in the center. The other types of
fishtail sprays deposite different profiles depending
upon the occurence and location of jets in the spray
pattern, but they share a common defect in that the
spray deposition is highly non-uniform, typically
with heavy deposition zones being separated by light
deposition zones. This, plus a lack of sufficiently
tapered edges, make it difficult to apply a uniform

coating. The fishtail sprays also characteristically have poor atomization and relatively large droplet sizes, which make it difficult to apply a high quality coating.

In complete contrast thereto, when the coating mixture is sprayed with the proper concentration of subcritical compressed fluid and pressure and temperature conditions such that vigorous decompressive atomization is obtained, a feathered spray deposition pattern is observed on a substrate coated with such a spray, which is diagrammatically illustrated in Figure 3. Figure 3 shows the margins of the spray pattern desirably containing less solid particles than in the center thereof. An actual feathered spray pattern typically deposits coating relatively uniformly in a wide central portion and deposits progressively less coating at the tapered edges. This feathering is particularly desirable for overlapping adjacent layers of sprayed coating to produce a coating film of uniform thickness. This is one of the principle reasons why air sprays are used instead of airless sprays to apply high-quality coatings.

Accordingly, as a way to determine whether a coating composition is being sprayed at the proper spraying conditions of temperature, pressure, amount of subcritical compressed fluid, and the like, such that good atomization is being obtained which results in a high-quality coating, it is generally sufficient to simply examine the visual appearance of the

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spray. If a feathered spray is observed, such as
those shown in Figure 5, then it can be reasonably
assumed that proper atomization is being obtained.
The presence of a fishtail pattern, however, is
generally indicative of poor atomization.

For a given coating composition and constant
spray temperature and pressure, the feathered spray
pattern is characteristically obtained when the
subcritical compressed carbon dioxide concentration
in the spray mixture exceeds a transition
concentration. With no carbon dioxide, the binding
forces of cohesion, surface tension, and viscosity in
the incompressible spray solution produce a typical
fishtail spray pattern with very poor liquid-film
atomization. At carbon dioxide concentrations below
the transition region, the binding force exceeds the
expansive force of the subcritical compressed carbon
dioxide, so a fishtail spray pattern persists, but it
becomes more uniform, the spray fan becomes wider,
the visible liquid film recedes towards the orifice,
and the spray mixture becomes compressible as the
concentration increases from zero. At the
mid-transition concentration, the expansive force
equals the binding force, so neither controls the
spray pattern. The visible liquid film has
disappeared and atomization is occurring at the spray
orifice. Surprisingly, as the concentration
increases through the transition region, the angular
flat fishtail spray fan typically first contracts
into a narrow transitional oval or flared non-planar
spray and then greatly expands into a much wider

parabolic flat feathered spray fan produced by
vigorous decompressive atomization. The transition
can be seen not only in the shape of the spray but
also in the greatly improved atomization and
deposition of the coating. The droplet size becomes
much smaller, which shows that the cohesive binding
force is completely overcome by the expansive force
of the subcritical compressed carbon dioxide, and
coating quality is greatly improved. At carbon
dioxide concentrations above the transition region,
the spray fan is fully feathered, typically much
wider and thicker, and exits the spray orifice at a
much greater angle. Higher concentration further
decreases the particle size, increases the fan width,
and makes the spray solution more highly
compressible, which affects the spray rate.
One manifestation of the expansive force of the
subcritical compressed carbon dioxide is that the
feathered spray typically has a much greater fan
width than normal airless sprays produced by the same
spray tip. Although the spray leaves the spray tip
at a much wider angle than normal airless sprays, the
fan width can be indexed to give any fan width from
narrow to very wide by changing the fan width rating
of the airless spray tip, as is normally done.

        For a given coating composition, at a
constant concentration of subcritical compressed
fluid, a transition from a fishtail liquid-film spray
to a feathered decompressive spray can frequently be
obtained by increasing the spray temperature and/or
decreasing the spray pressure. Increasing the

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temperature increases the driving force for
gasification of the subcritical compressed fluid as
the spray exits the spray orifice, but it also
decreases the solubililty. Therefore, an optimum
temperature exists. Decreasing the pressure lowers
the density of the compressibly spray mixture, which
lowers the cohesiveness, but it also decreases the
solubility. Therefore, an optimum pressure exists.
In general, the concentration of subcritical
compressed fluid, temperature, and pressure needed to
obtain a feathered decompressive spray depends upon
the properties of the coating composition being
sprayed and is determined experimentally.

     The ability to obtain a feathered
decompressive spray also depends upon the molecular
weight profile of the coating composition, as noted
above. Figures 7a and 7b illustrate the transition
that may occur from a feathered decompressive spray
to a fishtail liquid-film spray as the molecular
weight of the polymer system increases such as due to
catalyzed cross-linking reaction occurring in the
coating composition, with other factors remaining the
same. The coating composition is a clear air-dry
alkyd-urea catalyzed conversion coating that had a
polymer content of 69%, an initial alkyd
number-average molecular weight of 1,980, and an
intial viscosity of 1080 centipoise before catalyst
was added. Figure 7a shows the feathered
decompressive spray produced by a subcritical
compressed carbon dioxide concentration of about 30%,
a spray temperature of 26 C, and a spray pressure of

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900 psi, after reaction had proceeded for some time.
Figure 7b shows the fishtail liquid-film spray that
was produced after reaction had proceeded further and
the molecular weight had substantially increased, as
evident from the large increase in the viscosity of
the coating composition. However, the fishtail spray
remained even after adding diluent solvent to reduce
the viscosity to below its original level. This
shows that the transition was due to the increase in
molecular weight through reaction and not to the
increase in viscosity that this caused.

     One benefit of spraying at subcritical
ambient temperature is that the spray mixture may
contain a relatively large concentration of excess
subcritical compressed fluid above the solubility
limit, that is, forming a two-phase spray mixture,
without adversely affecting flow out of the deposited
coating, as would occur at elevated temperatures. At
ambient temperature, the organic solvents in the
coating composition would be much less volatile than
at temperatures of 50 to 60 C commonly used in
spraying with supercritical fluids. Therefore, much
less solvent would be extracted from the liquid
coating phase into the excess compressed fluid
phase. Therefore, subcritical compressed fluid may
be added in excess of the solubility limit in order
to obtain a feathered spray. An emulsion of liquid
subcritical compressed fluid with the liquid spray
mixture may be more desirable than a dispersion of
gaseous subcritical compressed fluid, because the
greater density of the liquid would cause less phase

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separation by settling and would have a greater expansive force density.

Turning now to a discussion of how to actually carry out the practice of the present invention, reference is made to Figure 1. An apparatus is shown which is capable of pumping, pressurizing, metering, proportioning, heating, and mixing a coating composition with carbon dioxide to form a liquid mixture comprising the coating composition and subcritical compressed carbon dioxide which is present in essentially precisely desired proportions ready for being sprayed. While the following discussion will be focused on carbon dioxide, it is not limited to this material and indeed, any subcritical compressed fluid, such as the ones discussed earlier, which are suitable for the particular application desired, may also be utilized.

In particular, carbon dioxide is supplied as a liquid from any suitable source, such as a tank or cylinder which is as denoted as 100 in the drawing. Preferably, the liquid carbon dioxide is supplied on a continuous basis from whatever source is utilized. The liquid carbon dioxide, at its vapor pressure at room temperature (approximately 830 psi) is introduced into a reciprocating pump 110 which in this embodiment is shown as a double-acting piston pump having four check valves.

In the present invention, it has been found that the reciprocating pump used to pump the liquid

carbon dioxide is desirably designed for a high feed
pressure. The high feed pressure should not cause a
change in outlet pressure during a pumping cycle.
Liquid carbon dioxide is normally stored in bulk at a
temperature of about $-18^{\circ}C$ ($0^{\circ}F$) and 300 psi vapor
pressure and in a cylinder at room temperature and
830 psi vapor pressure. Accordingly, the feed
pressure may vary from 300 to 830 psi, or higher.
Some double-acting pump designs (pumps that discharge
throughout their cycle and do not stop pumping during
the suction part of the cycle) are generally designed
for low feed pressures. Consequently, a high feed
pressure may affect the forces in the pump and alter
the outlet pressure during part of the pumping cycle.

Thus, a typical double-acting three check
valve piston pump should preferably not be used for
pumping the liquid carbon dioxide. Such a pump has
an inlet check valve at the bottom, an outlet check
valve at the top, and a check valve situated in the
piston·head, which allows liquid to flow from the
bottom compartment to the top compartment when the
piston is moving downward. On the downstroke, the
inlet check valve closes, fluid flows from the bottom
compartment to the top compartment through the check
valve in the piston, and fluid flows out the outlet
check valve, because the piston rod, which has half
the cross-sectional area of the piston, moves into
the pump cylinder and reduces its total volume. When
the piston moves upward, the check valve in the
piston closes, fluid flows out the outlet check valve
from the top compartment, and fluid flows in the

inlet check valve and fills the bottom compartment.
As a result of such operation, this pump is designed
for low feed pressure, typically below 100 psi, so
that the outlet pressure on the upstroke and
downstroke are nearly the same. If this kind of a
pump were operated with a high feed pressure of about
830 psi such as that associated with the liquid
carbon dioxide, the outlet pressure on the upstroke
would be about 1900 psi higher than the outlet
pressure on the downstroke since the inlet feed
pressure assists the pumping action on the upstroke
but not the downstroke. The pressure increase would
be twice the feed pressure due to the piston surface
area on the inlet side being twice the piston area on
the outlet side.

Accordingly, a double-acting piston pump
having four check valves which can accommodate a high
feed pressure is particularly suitable in the present
invention for pressurizing the liquid carbon
dioxide. Both the top and bottom compartments of
this type of pump each have an inlet and outlet check
valve, respectively. The piston does not have a
check valve. The piston rod extends through both
ends of the cylinder, with packing at both ends. The
pump design and operation is symmetrical in the
upstroke and downstroke directions, so that the
outlet pressure is the same in both parts of the
cycle. When the piston moves upward, fluid flows out
the upper outlet check valve and fluid flows in the
lower inlet check valve simultaneously. When the
piston then moves downward, fluid flow out the lower

outlet check valve while fluid flows in the upper
inlet check valve.

Pump 110 may be driven by any suitable
means. An air motor 112 supplied with air from lines
10, 12 and 14, respectively, may be utilized to give
pump-on-demand performance. Desirably, a circulating
refrigeration system (not shown) is used to cool pump
110 to help avoid cavitation. The carbon dioxide is
generally pumped to a pressure of about 1500 to about
1700 psi and then let down in pressure to the desired
spray pressure using a pressure regulator (not shown)
for a typical airless spray gun application.

Coating composition is continuously supplied
from any suitable source such as a pressure pot 114.
Although just one such pot is shown in the drawing,
it is understood that a plurality of such pots may be
used in series or parallel while others are
simultaneously being charged so as to provide the
desired continuous flow. The coating composition may
first be pumped by a pumping means 116 which in this
embodiment is a double-acting three check valve
reciprocating piston pump which has been described
earlier. An air motor 118 supplied with pressurized
air from lines 10, 16 and 18, respectively, may be
used to drive the pump. Such a reciprocating pump
may be used as a supplementary pump when a very
thick, viscous and/or abrasive coating composition is
being utilized. Otherwise, the coating composition
is pumped directly by precision gear pump 126.

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    After being pressurized by pump 110, the
carbon dioxide passes through a coriolis mass flow
meter 120 to measure the mass flow rate in a manner
described later with respect to Figure 2. The
measured mass flow rate is sensed by an electronic
receiving device 122 which in turn sends out an
electronic signal to electronic ratio controller 124,
which will be discussed later.

    Simultaneously, the coating composition is
being fed to precision gear pump 126 which is capable
of delivering precise amounts of the coating
composition on demand.

    The ratio controller 124 contains logic
circuitry which can be programmed to accept the
electronic signal from device 122 and in turn
generates a signal to pump 126 to control its speed.
Correspondingly, the amount of coating composition
that leaves pump 126 is substantially precisely
controlled to a predetermined ratio relative to the
amount of carbon dioxide measured by mass flow meter
120. The ratio controller works cooperatively with a
microprocessor 128 which also receives the mass flow
rate information from receiving device 122 and which
can also send information to the ratio controller
from a precision gear metering device 130 to which
the coating composition passes after being pumped by
gear pump 126.

The flow rate measured by metering device 130 generates a flow feedback signal which is electronically received by the microprocessor 128. The microprocessor compares the actual flow rate that is measured by metering device 130 with the required flow rate needed to provide the desired ratio of coating composition and carbon dioxide based on its preset programming and sends appropriate electronic instructions to the controller 124 to makes any adjustments needed to the speed of pump 126 so as to obtain that required flow rate.

A general purpose Molytek data logger 135 with mathematical capability may be utilized for data printing and calculations pertaining to the stream characteristics. Additionally, due to the burst mode of spraying that may be associated with the admixed liquid composition, a burst mode signal conditioning module 132 is also preferably utilized to permit evaluation of a single short spray burst, or a series or short spray bursts with interruptions.

After passing through the metering device 130, the coating composition is heated if desired by optional heater 134 which desirably is an electric high pressure paint heater in order to reduce its viscosity to aid in the mixing with the carbon dioxide. The coating composition is then preferably filtered in fluid filter 136 to remove particulates and fed through a check valve into mixing manifold 138 where it is joined in just the proper proportion

with the carbon dioxide after it too has passed
through a check valve and into mixing manifold 138.

After the coating composition and carbon
dioxide are accurately proportioned together at the
mixing manifold, it then enters into a circulation
loop generally denoted as 500 in the drawing. The
circulation loop continuously pumps, uniformly mixes,
and optionally heats the mixture of coating
composition and carbon dioxide such that the carbon
dioxide enters and remains well mixed and, moreover,
circulates the now admixed liquid mixture of coating
composition and subcritical compressed carbon dioxide
past a spraying means which is capable of spraying
the mixture on demand.

Particularly, once having entered the
circulation loop 500, the mixture is generally first
further mixed by means of a static mixer 140 which
helps provide a more uniform blend. The mixture then
passes through optional heater 142 to obtain the
desired spray temperature.

The admixed liquid mixture comprised of the
coating composition and subcritical compressed carbon
dioxide is then filtered once again in filter 144 and
passes through a Jerguson sight glass 146 which is
used to examine the phase condition of the admixed
liquid mixture. Circulation flow in the circulation
loop is obtained through the use of gear pump 148. A
pressure relief valve 150 is desirably provided to
protect the system from overpressurization.

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By the proper opening and closing of valves, the admixed liquid composition may be passed through a spraying device generally denoted as 600 in the drawing which may be operated manually on an on-demand basis by pulling a trigger on an airless or electrostatic airless spray gun, or automatically by a spray gun mounted on a reciprocator (not shown).

In a more preferred embodiment which is shown in Figure 2, the carbon dioxide is continuously supplied from a cryogenic carbon dioxide feed system shown generally as 2 in the drawing. The cryogenic carbon dioxide at approximately 300 psi is first fed to an air driven carbon dioxide primer pump (not shown) located at the carbon dioxide feed system 2 (Haskel Inc., Model AGD-15) for initial pressurization. The feed line in between the carbon dioxide source 2 and the primer pump is preferably insulated and also kept refrigerated by bleeding carbon dioxide (approximately 1/2 lb/hr) through a coil wrapped around the feed line. Surge tank 9 is provided to help damp flow fluctuations in the feed line. The carbon dioxide now having a pressure of between about 1000 to about 1400 psi, and after being filtered by in-line filter 8, is then pressurized to a pressure of about 1600 to about 1800 psig by a carbon dioxide liquid pump 10 (Haskel Inc., Model 8DSFD-25). This liquid pump is a single-acting pump that utilizes a three-way cycling spool that is designed for pumping liquified gases under pressure without requiring refrigeration to avoid cavitation.

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If desired, in order to help reduce flow fluctuations which may be caused by the single-acting pump, an accumulator (now shown) such as accumulator 43 or even another surge tank, such as surge tank 9, may be utilized immediately after this pump. Moreover, a double-acting pump having four check valves may alternatively be used, if desired. After passing through disposable in-line filter 13, the pressurized carbon dioxide is then regulated down with a pressure regulator 15 to the desired steady outlet pressure for spraying.

After being pressurized and regulated, carbon dioxide flows through coriolis meter 21 (Micro Motion, Inc., Model D6) for a true mass flow rate measurement. A capillary tube (1 ft x 1/16 in. OD) and a check valve (25 psi) connected in parallel at 20 is installed prior to the coriolis meter to help avoid a large carbon dioxide flow surge and to smooth down the carbon dioxide flow rate when the liquid pump 10 is activated. A Hoke global valve and a capillary tubing (7 ft x 1/16 in. OD) connected in series at 25 is used to control and restrict the carbon dioxide flow during the initial start-up. After the system is pressurized, another Hoke global valve 26 is opened to allow steady carbon dioxide flow for normal operation. A pressure relief valve 12 (Anderson Greenwood) is used to protect the carbon dioxide system from overpressurization.

The coating composition is fed from a coating supply system generally shown as 3 in the

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drawing. An accumulator 14 using nitrogen is
utilized to offset any pressure pulsation. The
coating flow rate is metered by a precision gear pump
18 (Zenith, Model HLB-5592). Viscous coating from
coating supply system 3 is normally pressurized with
a booster pump (not shown) to provide sufficient flow
through filters and feed lines to the Zenith metering
pump to avoid cavitation. Such a booster pump may
include a liquid pump such as a Haskel type pump
similar to pump 10. The Zenith pump 18 supplies the
positive pressure needed for feeding the coating
composition to the recirculation loop. A precision
gear meter 24 (AW Co., Model ZHM-02) is used for
measuring the flow rate of the coating composition.
The speed command of the Zenith pump is
electronically controlled by the ZeDrive Speed
Control System 17 that receives the input signal from
the Micro Motion remote electronics unit 16. The
coating metering rate is electronically adjusted by
coating flow feedback signal received from the gear
meter 24. The desired carbon dioxide mass ratio is
therefore maintained when the two feeds are combined
at the entrance to the circulation loop at manifold
39. As an alternative embodiment, instead of
electronically controlling the Zenith pump, the
control system 17 may be made to adjust an air drive
control valve (not shown) which would regulate an
amount of pressurized air that would be available to
a pump air drive system which is connected to the
pump.

The coating composition flows through
optional heater 31 (Binks heater) and a paint filter
32 (Binks paint filter) before it enters the
circulation loop. Pressure relief valve 29 (Anderson
Greenwood) is used to protect the coating composition
system from overpressurization.

A multi-channel flow computer 22 (AW Co.,
Model EMO-1005) is used for both instantaneous and
cumulative flow rate computation/indication. A
general purpose Molytek data logger 27 with
mathematical capability provides data printing and
calculation functions of the characteristics of the
two streams.

The coating composition and carbon dioxide
are combined at manifold 39 and passed through a
static mixer 40 (Binks) before entering the
circulation loop. The check valves 36 and 37 prevent
back flow of the two fluids. The combined mixture is
then again mixed in another static mixer 41 (Binks)
in the circulation loop itself. The mixture is
optionally heated and controlled to the desired
temperature in the circulation loop through two
respective sets of optional high pressure heaters 45
and 65, both connected in series. The mixture also
flows through two filters 47 and 66 and is circulated
in the loop by a gear pump 61 (Zenith, Model
HLB-5592). If desired, the circulation return
portion of the loop from spraying means 100 to the
inlet at mixer 40 may be eliminated if spraying is at
ambient temperature and circulation is not desired.

An accumulator 43 (Tobul, Model 4.7A30-4) is
used to increase the loop capacity and also used to
minimize the pressure pulsation in the loop when
spray system 100 is activated. Pressure relief
valves 53 and 63 (Anderson Greenwood) are used to
protect the loop from overpressurization. A sight
glass 50 (Jerguson) is used to view the mixture in
the loop and observe its phase. A mass flow meter 54
(Micro Motion Inc., Model D12) is used to monitor the
fluid density and flow rate in the circulation loop.
The admixed liquid mixture is sprayed onto the
substrates from spray system 100.

EXAMPLES

Example 1

A coating formulation that has a solids
content of 75.87% and a viscosity of 1100 centipoise
(23 C) and that gives a clear acrylic coating was
prepared from Rohm & Haas Acryloid[tm] AT-954 resin,
which contains 85% nonvolatile acrylic polymer
dissolved in 15% methyl amyl ketone solvent, and
American Cyanamid Cymel[tm] 323 resin, which is a
cross-linking agent that contains 80% nonvolatile
melamine polymer dissolved in 20% isobutanol, solvent,
by mixing the resins with solvents ethyl
3-ethoxypropionate (EEP) and acetone and with 50%
Union Carbide silicone surfactant L7605 dissolved in
xylene, in the following proportions:

Acryloid AT-954	10,500.0 g	67.48%
Cymel 323	3,600.0 g	23.14%
EEP	840.0 g	5.40%
acetone	560.0 g	3.60%
50% L7605 in xylene	60.0 g	0.38%
Total	15,560.0 g	100.00%

The acrylic and melamine polymers had the following
molecular weights:

<u>Acryloid AT-954</u>

Molecular weight	6,070 weight average (Mw)
Molecular weight	1,670 number average (Mn)
Mw/Mn	3.63

<u>Cymel 323</u>

Molecular weight	490 weight average (Mw)
Molecular weight	410 number average (Mn)
Mw/Mn	1.20

The coating formulation contained 75.87% solids
fraction and 24.13% solvent and surfactant fraction,
with the following component composition:

AT-954 polymer	8,925.0 g	57.36%
Cymel 323 polymer	2,880.0 g	18.51%
methyl amyl ketone	1,575.0 g	10.12%
EEP	840.0 g	5.40%
isobutanol	720.0 g	4.63%
acetone	560.0 g	3.60%
xylene	30.0 g	0.19%
L5310	30.0 g	0.19%
Total	15,560.0 g	100.00%

The solids fraction had the following composition:

AT-954 polymer	8,925.0 g	75.60%
Cymel 323 polymer	2,880.0 g	24.40%
Total	11,805.0 g	100.00%

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The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
acetone	560.0 g	15.03%	1440
isobutanol	720.0 g	19.33%	74
xylene	30.0 g	0.81%	70
methyl amyl ketone	1,575.0 g	42.28%	40
EEP	840.0 g	22.55%	11
Total	3,725.0 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	65%
50 to 100	20%
101 to 250	0%
ï 250	15%

The coating formulation had the following properties:

Solvent content	247	grams/liter
Relative evap. rate	29	(butyl acetate = 100)
Viscosity	1100	centipoise (23 C)
Weight solids	75.87	percent
Liquid density	1023	grams/liter

Spray experiments were done using
Bonderite[tm] 37 polished 24-gauge steel test panels,
6-inch by 12-inch size. The test panels were

sprayed, flashed, and baked in a vertical
orientation. Coating thickness was measured using a
Microtest[tm] III Magnetic Coating Thickness Meter
(Paul N. Gardner Company, Pompano Beach, Florida).
Coating gloss was measured using a Macbeth[tm]
Novo-Gloss 20-degree Glossmeter (Paul N. Gardner
Company, Pompano Beach, Florida). Coating
distinctness of image (DOI) was measured using a
Model #300 Distinctness of Image Meter (Mechanical
Design and Engineering Company, Burton, Michigan)
and a Model #1792 Distinctness of Reflected Image
Meter (ATI Systems, Madison Heights, Michigan).

A spray mixture was prepared and sprayed in
the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. The spray mixture had a compressed carbon
dioxide content of 29.2% by weight.

The spray mixture was sprayed using a
Nordson A7A airless automatic spray gun with Spraying
Systems tip #400011, which has a 9-mil orifice size,
a 40-degree spray angle rating, and a 7-inch fan
width rating, and with Spraying Systems minimum
cavity tip insert #15153-NY. The distance from the
spray tip to the panel was twelve inches. Panels
were sprayed using a Model #310540 Automatic Test
Panel Spray Unit (Spraymation, Fort Lauderdale,
Florida).

At a spray temperature equal to the ambient
temperature of 24.0 C and at a spray pressure of 1600
psi, a fishtail spray pattern was produced with
atomization occurring from a visible liquid-film that
extended from the spray orifice. The spray fan was
angular in shape and had a fan width of about nine
inches. Decreasing the spray pressure to 900 psi
produced a spray pattern in transition between a
fishtail spray and a feathered spray. The liquid
film was no longer visible. Increasing the spray
temperature to 27.4 C at a spray pressure of 900 psi
produced a much wider fully feathered flat spray fan
that was parabolic in shape and that left the orifice
at a very large angle. The fan width was about 14
inches.

At the spray temperature of 27.4 C,
compressed carbon dioxide has a vapor pressure of 984
psi and has equilibrium gas and liquid densities of
0.27 and 0.66 g/cc, respectively. Therefore, at the
spray pressure of 900 psi, the spray mixture
contained coating formulation admixed with compressed
carbon dioxide gas. The spray mixture was a clear
single-phase liquid solution. Therefore, all of the
compressed carbon dioxide gas was dissolved in the
coating formulation.

Panels were sprayed at the above conditions
using a spray index distance of three inches and
various spray traverse rates to produce coatings of
various thickness. The panels were flashed for
several minutes and then baked in an oven at a

temperature of 125 C for at least thirty minutes.
The baked coatings had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.0 mil	90%	80%	48%
1.0 mil	91%	80%	52%
1.4 mil	91%	85%	56%
1.5 mil	92%	85%	60%
1.8 mil	92%	90%	68%
2.0 mil	93%	90%	72%
2.5 mil	95%	90%	73%
2.5 mil	95%	90%	75%
3.0 mil	94%	90%	76%
3.0 mil	94%	92%	78%

Panels were also sprayed at a spray temperature of
28.0 C and a spray pressure of 900 psi. These
coatings had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.1 mil	90%	80%	53%
1.4 mil	90%	85%	58%
1.7 mil	94%	90%	67%
2.4 mil	94%	90%	77%
3.5 mil	94%	92%	79%

The polymeric coatings were clear and had very good
appearance. They were very smooth with high gloss

and high distinctness of image. They were free of
haze and bubbles and even the very thick coatings did
not run or sag or have solvent popping.

Example 2

A coating formulation that has a solids
content of 74.77% and a viscosity of 1340 centipoise
(23 C) and that gives a clear acrylic coating was
prepared from Acryloid^{tm} AT-954 resin and Cymel^{tm} 323
resin by mixing the resins with solvents ethyl
3-ethoxypropionate (EEP) and methyl amyl ketone and
with 50% surfactant L7605 in xylene, in the following
proportions:

Acryloid AT-954	10,500.0 g	66.50%
Cymel 323	3,600.0 g	22.80%
EEP	840.0 g	5.32%
methyl amyl ketone	789.5 g	5.00%
50% L7605 in xylene	60.0 g	0.38%
Total	15,789.5 g	100.00%

The acrylic polymer had the following molecular
weight:

Molecular weight	6,070 weight average (Mw)
Molecular weight	1,670 number average (Mn)
Mw/Mn	3.63

The coating formulation contained 74.77% solids
fraction and 25.23% solvent and surfactant fraction,

with the following component composition:

AT-954 polymer	8,925.0 g	56.53%
Cymel 323 polymer	2,880.0 g	18.24%
methyl amyl ketone	2,364.5 g	14.97%
EEP	840.0 g	5.32%
isobutanol	720.0 g	4.56%
xylene	30.0 g	0.19%
L5310	30.0 g	0.19%
Total	15,789.5 g	100.00%

The solids fraction had the following composition:

AT-954 polymer	8,925.0 g	75.60%
Cymel 323 polymer	2,880.0 g	24.40%
Total	11,805.0 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isobutanol	720.0 g	18.21%	74
xylene	30.0 g	0.76%	70
methyl amyl ketone	2,364.5 g	59.79%	40
EEP	840.0 g	21.24%	11
Total	3,954.5 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

```
            <  50        81%
        50 to 100        19%
       101 to 250         0%
           ï 250          0%
```

The coating formulation had the following properties:

```
    Solvent content          258 grams/liter
    Relative evap. rate        27 (butyl acetate = 100)
    Viscosity                1340 centipoise (23 C)
    Weight solids           74.77 percent
    Liquid density           1021 grams/liter
```

Spray mixtures were prepared and sprayed in the continuous mode by admixing the coating formulation with the desired proportion of compressed carbon dioxide, both pressurized to the desired spray pressure. The spray mixtures had compressed carbon dioxide contents of 28-30% by weight.

The spray mixtures were sprayed at or near ambient temperature (24-26 C) with spray pressures of 900-950 psi using a Nordson A7A airless automatic spray gun with a variety of airless spray tips from several manufacturers and having a range of orifice sizes and fan width ratings. The distance from the spray tip to the panel was twelve inches. Panels were sprayed using a Spraymation automatic sprayer. The sprays were all feathered flat spray fans that were parabolic in shape and that left the orifice at a very large angle. The panels were flashed for

several minutes and then baked in an oven at a
temperature of 125 C for at least thirty minutes.

At the spray temperatures used, compressed
carbon dioxide has the following vapor pressures and
equilibrium gas and liquid densities:

	Vapor	Gas	Liquid
Temperature	Pressure	Density	Density
24 C	908 psi	0.23 g/cc	0.72 g/cc
25 C	930 psi	0.24 g/cc	0.70 g/cc
26 C	951 psi	0.25 g/cc	0.69 g/cc

Therefore, at all the combinations of spray
temperatures and pressures used, the spray mixtures
contained coating formulation admixed with compressed
carbon dioxide that was at or very near the
equilibrium conditions where gas and liquid exist
together. The spray mixtures were clear single-phase
liquid solutions. Therefore, all of the compressed
carbon dioxide mixture of gas and liquid was
dissolved in the coating formulation.

At a spray temperature of 25 C and a spray
pressure of 950 psi, coatings with different
thicknesses were sprayed using the following Spraying
Systems tips: 1) tip #250004, which has a 5-mil
orifice size, a 25-degree fan angle rating, and a
5-inch fan width rating, and 2) tip #400006, which
has a 6-mil orifice size, a 40-degree fan angle
rating, and a 6.5-inch fan width rating. Minimum

cavity insert #15153-NY was used in each tip. The
coatings had the following properties:

Tip	Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1	0.3 mil	70%	70%	33%
1	0.7 mil	86%	80%	46%
1	1.2 mil	91%	90%	70%
1	2.6 mil	92%	90%	73%
2	0.3 mil	40%	50%	12%
2	0.7 mil	85%	75%	43%
2	1.1 mil	91%	85%	58%
2	1.2 mil	91%	85%	56%
2	2.0 mil	94%	90%	73%

At a spray temperature of 25 C and a spray
pressure of 950 psi, coatings were sprayed using the
following spray tips, each of which has a 7-mil
orifice size: 1) Binks tip #9-0730, which has a
25-degree fan angle rating and a 5.5-inch fan width
rating, 2) Nordson tip #0003-06 with turbulence plate
#027-003, which has a 30-degree fan angle rating and
a 6-inch fan width rating, and 3) Binks tip #9-0740,
which has a 40-degree fan angle rating and a 6.5-inch
fan width rating. The coatings had the following
properties:

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Tip	Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1	0.4 mil	47%	55%	18%
1	0.7 mil	84%	70%	40%
1	1.0 mil	91%	85%	57%
1	1.4 mil	91%	85%	54%
1	1.6 mil	93%	90%	75%
2	1.0 mil	90%	80%	48%
2	1.3 mil	92%	80%	53%
2	1.6 mil	92%	90%	66%
3	0.4 mil	64%	55%	18%
3	0.8 mil	87%	80%	46%
3	1.4 mil	92%	85%	60%
3	1.5 mil	91%	85%	58%
3	1.8 mil	93%	90%	76%

At a spray temperature of 24 C and a spray
pressure of 900 psi, coatings were sprayed using the
following spray tips, each of which has a 9-mil
orifice size: 1) Spraying Systems tip #400011 with
insert #15153-NY, which has a 40-degree fan angle
rating and a 7-inch fan width rating and 2) Graco tip
#163-409, which has a 50-degree fan angle rating and
a 9-inch fan width rating. The coatings had the
following properties:

| | | Coating | 20-Degree | | |
Tip	Thickness		Gloss	MDEC DOI	ATI DOI
1	1.0 mil		88%	80%	49%
1	1.6 mil		93%	90%	74%
1	1.6 mil		94%	90%	74%
2	1.1 mil		88%	75%	45%
2	1.6 mil		93%	90%	66%
2	2.5 mil		94%	90%	73%

At a spray temperature of 26 C and a spray pressure of 950 psi, coatings were sprayed using Spraying Systems tip #400011 with insert #15153-NY, which has a 40-degree fan angle rating and a 7-inch fan width rating. The coatings had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.6 mil	78%	65%	31%
1.3 mil	91%	80%	51%
1.5 mil	91%	85%	55%
1.8 mil	94%	90%	72%
2.5 mil	94%	85%	65%
3.0 mil	95%	85%	62%

The polymeric coatings were clear and had very good appearance. They were smooth with high gloss and high distinctness of image. They were free of haze

and bubbles and even the very thick coatings did not
run or sag or have solvent popping.

Example 3

The coating formulation and spray mixture
used in Example 2 was sprayed at a temperature of 26
C and a pressure of 950 psi using a Graco AA3000
air-assist airless automatic spray gun with tip #309,
which has a 9-mil orifice size and a 7-inch fan width
rating. Coatings were sprayed to different
thicknesses using no air assist and using air-assist
at different air pressures. The coatings had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI	Air Pressure
0.9 mil	83%	80%	47%	0 psi
1.7 mil	93%	85%	62%	0 psi
2.3 mil	88%	85%	55%	0 psi
2.8 mil	90%	80%	52%	0 psi
3.4 mil	95%	90%	76%	0 psi
1.2 mil	91%	80%	53%	10 psi
2.0 mil	93%	90%	72%	10 psi
2.5 mil	92%	90%	74%	10 psi
3.0 mil	94%	90%	70%	10 psi
3.5 mil	93%	90%	73%	10 psi

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1.5 mil	92%	85%	55%	20 psi
2.3 mil	93%	90%	72%	20 psi
3.3 mil	94%	90%	75%	20 psi
3.6 mil	93%	90%	77%	20 psi
2.4 mil	94%	85%	65%	30 psi
3.5 mil	94%	85%	64%	30 psi
3.8 mil	92%	90%	69%	30 psi
4.0 mil	94%	90%	76%	30 psi

The polymeric coatings were clear and had good
appearance. They were smooth with high gloss and
good distinctness of image. They were free of haze
and bubbles and did not run or sag or have solvent
popping.

Example 4

A coating formulation that has a solids
content of 68.75% and a viscosity of 940 centipoise
(23 C) and that gives a clear acrylic coating was
prepared from Acryloid^{tm} AT-954 resin and Cymel^{tm} 323
resin by mixing the resins with solvents methyl
isobutyl ketone (MIBK), ethyl 3-ethoxypropionate
(EEP), and methyl amyl ketone and with 50% surfactant
L7605 dissolved in xylene, in the following
proportions:

Acryloid AT-954	10,500.0 g	61.16%
Cymel 323	3,600.0 g	20.97%
MIBK	1,545.0 g	9.00%

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EEP	840.0 g	4.89%
methyl amyl ketone	625.0 g	3.64%
50% L7605 in xylene	60.0 g	0.35%
Total	17,170.0 g	100.00%

The acrylic polymer had the following molecular weight:

Acryloid AT-954

Molecular weight	6,070 weight average (Mw)
Molecular weight	1,670 number average (Mn)
Mw/Mn	3.63

The coating formulation contained 68.75% solids fraction and 31.25% solvent and surfactant fraction, with the following component composition:

AT-954 polymer	8,925.0 g	51.98%
Cymel 323 polymer	2,880.0 g	16.77%
methyl amyl ketone	2,200.0 g	12.81%
MIBK	1,545.0 g	9.00%
EEP	840.0 g	4.89%
isobutanol	720.0 g	4.19%
xylene	30.0 g	0.18%
L5310	30.0 g	0.18%
Total	17,170.0 g	100.00%

The solids fraction had the following composition:

AT-954 polymer	8,925.0 g	75.60%
Cymel 323 polymer	2,880.0 g	24.40%
Total	11,805.0 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
MIBK	1,545.0 g	28.96%	162
isobutanol	720.0 g	13.50%	74
xylene	30.0 g	0.56%	70
methyl amyl ketone	2,200.0 g	41.23%	40
EEP	840.0 g	15.75%	11
Total	5,335.0 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	57%
50 to 100	14%
101 to 250	29%
ï 250	0%

The coating formulation had the following properties:

Solvent content	312	grams/liter
Relative evap. rate	35	(butyl acetate = 100)
Viscosity	940	centipoise (23 C)
Weight solids	68.75	percent
Liquid density	997	grams/liter

A spray mixture was prepared and sprayed in
the continuous mode by admixing the coating
formulation with the desired proportion of compressed

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carbon dioxide, both pressurized to the desired spray
pressure. The spray mixture had a compressed carbon
dioxide content of 26.6% by weight.

The spray mixture was sprayed at the ambient
temperature of 25.5 C and at a spray pressure of 950
psi using a Nordson A7A airless automatic spray gun
with Binks tip #9-0940, which has a 9-mil orifice
size, a 40-degree spray angle rating, and a 7-inch
fan width rating, and with Spraying Systems tip
insert #15153-NY. The distance from the spray tip to
the panel was twelve inches. Panels were sprayed
using a Spraymation automatic sprayer.

At the spray temperature of 25.5 C,
compressed carbon dioxide has a vapor pressure of 940
psi and has equilibrium gas and liquid densities of
0.25 and 0.70 g/cc, respectively. Therefore, at the
spray pressure of 950 psi, the spray mixture
contained coating formulation admixed with compressed
carbon dioxide that was on the liquid side of the
equilibrium conditions. The spray mixture was a
clear single-phase liquid solution. Therefore, all
of the liquid compressed carbon dioxide was dissolved
in the coating formulation.

The spray mixture produced a wide feathered
flat spray fan that was parabolic in shape and that
left the orifice at a very large angle. The fan
width was about 12 inches. Panels were sprayed and
the baked coatings had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.5 mil	72%	65%	29%
0.9 mil	91%	80%	50%
1.0 mil	92%	80%	55%
1.0 mil	92%	80%	52%
1.1 mil	90%	80%	47%
1.2 mil	91%	80%	53%
1.4 mil	95%	85%	62%

The polymeric coatings were clear, thin, smooth, free of haze and bubbles, and had good appearance and high gloss.

Example 5

    The coating formulation, spray mixture, and spray conditions used in Example 4 were used with a Graco AA3000 air-assist airless automatic spray gun with tip #309, which has a 9-mil orifice size and a 7-inch fan width rating. The spray produced a fan width of about 14 inches. Coatings were sprayed without and with air assist and they had the following properties:

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Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI	Air Pressure
1.3 mil	91%	85%	63%	0 psi
1.5 mil	93%	85%	63%	10 psi
1.8 mil	94%	80%	47%	10 psi
2.2 mil	93%	80%	52%	10 psi
2.5 mil	94%	80%	60%	10 psi

The polymeric coatings were clear, smooth, free of haze and bubbles, and had good appearance and high gloss.

Example 6

A coating formulation that has a solids content of 76.50% and a viscosity of 1800 centipoise and that gives a clear acrylic coating was prepared from Acryloid[tm] AT-954 resin and Cymel[tm] 323 resin by mixing the resins with solvents ethyl 3-ethoxypropionate (EEP) and methyl amyl ketone and with 50% surfactant L7605 in xylene, in the following proportions:

Acryloid AT-954	10,500.0 g	68.04%
Cymel 323	3,600.0 g	23.33%
EEP	840.0 g	5.44%
methyl amyl ketone	431.5 g	2.80%
50% L7605 in xylene	60.0 g	0.39%
Total	15,431.5 g	100.00%

The acrylic polymer had the following molecular weight:

Molecular weight	6,070 weight average (Mw)
Molecular weight	1,670 number average (Mn)
Mw/Mn	3.63

The coating formulation contained 76.50% solids fraction and 23.50% solvent and surfactant fraction, with the following component composition:

AT-954 polymer	8,925.0 g	57.84%
Cymel 323 polymer	2,880.0 g	18.67%
methyl amyl ketone	2,006.5 g	13.00%
EEP	840.0 g	5.44%
isobutanol	720.0 g	4.67%
xylene	30.0 g	0.19%
L5310	30.0 g	0.19%
Total	15,431.5 g	100.00%

The solids fraction had the following composition:

AT-954 polymer	8,925.0 g	75.60%
Cymel 323 polymer	2,880.0 g	24.40%
Total	11,805.0 g	100.00%

The solvent fraction had the following composition and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isobutanol	720.0 g	20.02%	74
xylene	30.0 g	0.83%	70
methyl amyl ketone	2,006.5 g	55.79%	40
EEP	840.0 g	23.36%	11
Total	3,596.5 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	79%	
50 to 100	21%	
101 to 250	0%	
ï 250	0%	

The coating formulation had the following properties:

Solvent content	241 grams/liter
Relative evap. rate	26 (butyl acetate = 100)
Viscosity	1800 centipoise
Weight solids	76.50 percent
Liquid density	1025 grams/liter

Spray mixtures were prepared and sprayed in
the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. Spray mixtures were used with compressed
carbon dioxide contents of 31%, 30%, and 29% by
weight.

Spraying was done under identical conditions
to compare airless spraying 1) with no air assist,
using the Nordson A7A automatic gun with Binks tip
#9-0940, and 2) with air assist, using the Graco
AA3000 automatic gun with tip #309. Both tips have a
9-mil orifice size and a 7-inch fan width rating.
Panels were sprayed in an identical manner using the
Spraymation automatic sprayer.

With a compressed carbon dioxide
concentration of 31%, at the ambient temperature of
24 C and a spray pressure of 900 psi, the sprays were
in transition between a fishtail spray and a
feathered spray. Increasing the spray temperature to
27 C produced feathered parabolic-shaped sprays with
fan widths of 12-14 inches. At this temperature,
compressed carbon dioxide has a vapor pressure of 973
psi and has equilibrium gas and liquid densities of
0.27 and 0.67 g/cc, respectively. Therefore, at the
spray pressure of 900 psi, the spray mixture
contained coating formulation admixed with compressed
carbon dioxide gas. The concentration of carbon
dioxide in the spray mixture was at the solubility
limit for these conditions. Coatings were sprayed
first using the Nordson gun (no air assist) and then
the Graco gun (air assist). The coatings had the
following properties:

Gun	Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI	Air Pressure
1	1.8 mil	88%	80%	50%	0 psi
2	1.8 mil	90%	85%	64%	5 psi
2	1.9 mil	91%	90%	66%	15 psi

The coatings sprayed with air assist had noticeably better appearance.

Increasing the spray temperature to 28 C at a spray pressure of 900 psi produced a two-phase spray mixture. At this temperature, compressed carbon dioxide has a vapor pressure of 995 psi and has equilibrium gas and liquid densities of 0.28 and 0.65 g/cc, respectively. Therefore, the spray mixture contained coating formulation admixed with compressed carbon dioxide gas in excess of the solubility limit, so that gas bubbles were finely dispersed in the liquid spray mixture. The coatings had the following properties:

Gun	Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI	Air Pressure
1	1.8 mil	90%	80%	49%	0 psi
2	2.0 mil	89%	85%	55%	5 psi
2	2.0 mil	90%	85%	63%	15 psi

The coatings sprayed with air assist had noticeably better appearance.

Decreasing the carbon dioxide concentration
to 30% at the spray temperature of 28 C and spray
pressure of 900 psi brought the spray mixture back to
the carbon dioxide solubility limit, as seen by just
a trace of fine gas bubbles. The coatings had the
following properties:

Gun	Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI	Air Pressure
1	1.8 mil	90%	80%	52%	0 psi
2	1.8 mil	90%	85%	55%	5 psi
2	1.8 mil	91%	85%	63%	15 psi

The coatings sprayed with air assist had noticeably
better appearance.

Decreasing the carbon dioxide concentration
to 30% and increasing the spray temperature to 29 C
at the spray pressure of 900 psi produced a clear
single-phase spray mixture. At this temperature,
compressed carbon dioxide has a gas pressure of 1017
psi and has equilibrium gas and liquid densities of
0.30 and 0.63 g/cc, respectively. Therefore, the
spray mixture contained coating formulation admixed
with compressed carbon dioxide gas in an amount below
the solubility limit at these conditions. The
coatings had the following properties:

Gun	Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI	Air Pressure
1	1.7 mil	89%	80%	51%	0 psi
2	1.9 mil	92%	85%	59%	5 psi
2	1.9 mil	90%	85%	62%	15 psi

The coatings sprayed with air assist had noticeably better appearance.

Example 7

A coating formulation that has a high solids content of 78.70% and a high viscosity of 3000 centipoise and that gives a clear acrylic coating was prepared by mixing Acryloid^{tm} AT-954 resin and Cymel^{tm} 323 resin with ethyl 3-ethoxypropionate (EEP) solvent and with 50% surfactant L7605 in xylene, in the following proportions:

Acryloid AT-954	10,500.0 g	70.00%
Cymel 323	3,600.0 g	24.00%
EEP	840.0 g	5.60%
50% L7605 in xylene	60.0 g	0.40%
Total	15,000.0 g	100.00%

The acrylic polymer had the following molecular weight:

Molecular weight	6,070 weight average (Mw)
Molecular weight	1,670 number average (Mn)
Mw/Mn	3.63

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The coating formulation contained 78.70% solids fraction and 21.30% solvent and surfactant fraction, with the following component composition:

AT-954 polymer	8,925.0 g	59.50%
Cymel 323 polymer	2,880.0 g	19.20%
methyl amyl ketone	1,575.0 g	10.50%
EEP	840.0 g	5.60%
isobutanol	720.0 g	4.80%
xylene	30.0 g	0.20%
L5310	30.0 g	0.20%
Total	15,000.0 g	100.00%

The solids fraction had the following composition:

AT-954 polymer	8,925.0 g	75.60%
Cymel 323 polymer	2,880.0 g	24.40%
Total	11,805.0 g	100.00%

The solvent fraction had the following composition and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isobutanol	720.0 g	22.75%	74
xylene	30.0 g	0.95%	70
methyl amyl ketone	1,575.0 g	49.76%	40
EEP	840.0 g	26.54%	11
Total	3,165.0 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

	< 50	76%
50 to 100		24%
101 to 250		0%
	ï 250	0%

The coating formulation had the following properties:

Property	Value	
Solvent content	219	grams/liter
Relative evap. rate	25	(butyl acetate = 100)
Viscosity	3000	centipoise
Weight solids	78.70	percent
Liquid density	1030	grams/liter

Spray mixtures were prepared and sprayed in
the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. Spraying was done using either 1) the
Nordson A7A airless spray gun with Binks tip #9-0940
or 2) the Graco AA3000 air-assist airless spray gun
with tip #309. Both tips have a 9-mil orifice size
and a 7-inch fan width rating. Panels were sprayed
using the Spraymation automatic sprayer.

With a carbon dioxide concentration of 28%
by weight, at the ambient temperature of 23.5 C and a
spray pressure of 1700 psi, both spray guns produced
a fishtail spray pattern with atomization occurring
from a visible liquid-film that extended from the

spray orifice. The spray fan was angular in shape
and had a fan width of 7 inches for the Nordson gun
and 9 inches for the Graco gun, with and without air
assist. Spraying panels produced coatings that were
thick layers of foam, which persisted through
flashing and baking. Decreasing the spray pressure
to 1500 psi produced the same results. Decreasing
the spray pressure to 1300 psi produced the same
result for the Graco gun but the spray from the
Nordson gun entered into transition from a fishtail
to a feathered spray and became a three-pronged jet
with a width of 7 inches and no visible liquid film.
Decreasing the spray pressure to 1100 psi narrowed
the jetting from the Nordson gun to a width of 4
inches. The spray from the Graco gun entered
transition and narrowed to a width of 3 inches with
no air assist but maintained a width of 8 inches with
an air-assist pressure of 20 psi. Decreasing the
spray pressure to 900 psi produced a two- pronged jet
with a width of 2 inches from the Nordson gun and
produced a single jet with a width of 1 inch from the
Graco gun, both with and without air assist. The
narrow jets were transformed into wide feathered
sprays at the spray pressure of 900 psi by either 1)
increasing the spray temperature to 28 C at the same
carbon dioxide concentration of 28% or 2) increasing
the spray temperature to 25 C and increasing the
carbon dioxide concentration to 30%.

At a carbon dioxide concentration of 28%,
spray temperature of 28 C, and spray pressure of 900
psi, the Nordson gun produced a wide feathered flat

spray fan that was parabolic in shape, that left the
orifice at a very large angle, and that was uniform
and had no jetting. The fan width was 12 inches.
The spray mixture contained two phases. At this
temperature, compressed carbon dioxide has a vapor
pressure of 995 psi and has equilibrium gas and
liquid densities of 0.28 and 0.65 g/cc,
respectively. Therefore, the spray mixture contained
coating formulation admixed with compressed carbon
dioxide gas in excess of the solubility limit, so
that gas bubbles were finely dispersed in the liquid
spray mixture. A coating was sprayed that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
2.3 mil	87%	80%	52%

The coating was smooth, glossy, and free of haze and
bubbles. Increasing the spray pressure to 1000 psi,
which equals the vapor pressure of carbon dioxide at
this temperature, produced a clear single-phase spray
solution. Therefore, the spray solution contained
coating formulation admixed with compressed carbon
dioxide that was at the equilibrium condition where
gas and liquid exist together. All of the compressed
carbon dioxide mixture of gas and liquid was
dissolved in the coating formulation. Coatings were
sprayed that had the following properties:

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Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
2.3 mil	92%	85%	64%
2.0 mil	92%	90%	71%

The coatings were smooth, glossy, and free of haze and bubbles. Increasing the spray pressure to 1100 psi, to 1200 psi, to 1300 psi, and then to 1500 psi continued to produce a feathered spray, but jetting appeared in the center of the spray that extended farther from the orifice as the pressure was increased before it dissipated. These pressures exceed the vapor pressure of carbon dioxide at this temperature, so the spray solution contained coating formulation admixed with liquid carbon dioxide. At a pressure of 1500 psi a coating was sprayed with the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
3.0 mil	88%	90%	68%

The coating was sprayed in the same manner as at the lower pressures and therefore the increased coating thickness was due to the greater spray rate at higher pressure. The coating was smooth, glossy, and free of haze and bubbles. The Graco gun was not used at these conditions.

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At a carbon dioxide concentration of 30%,
spray temperature of 25 C, and spray pressure of 900
psi, both spray guns produced wide feathered flat
spray fans that were parabolic in shape, that left
the orifice at very large angles, and that were
uniform and had no jetting. The fan width was about
10 inches for the Nordson gun and about 14 inches
inches for the Graco gun. The spray mixture was a
clear single-phase solution. At this temperature,
compressed carbon dioxide has a vapor pressure of 930
psi and has equilibrium gas and liquid densities of
0.24 and 0.70 g/cc, respectively. Therefore, the
spray mixture contained coating formulation admixed
with compressed carbon dioxide gas that was
completely dissolved. Coatings were sprayed that had
the following properties:

| | Coating | 20-Degree | | | Air |
Gun	Thickness	Gloss	MDEC DOI	ATI DOI	Pressure
1	1.3 mil	86%	75%	43%	0 psi
2	1.9 mil	86%	75%	42%	0 psi
2	2.1 mil	88%	80%	47%	10 psi
2	1.9 mil	89%	80%	47%	30 psi

The coatings were smooth, glossy, and free of haze
and bubbles.

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Example 8

A pigmented coating formulation that has a very high solids content of 81.44% and a viscosity of 540 centipoise (23 C) and that gives a white acrylic coating was prepared from Acryloid[tm] AT-954 resin and Cymel[tm] 323 resin by mixing the resins with Dupont Ti-pure[tm] 960 titanium dioxide pigment, with solvents methyl amyl ketone and acetone, and with Union Carbide silicone surfactant L7602, in the following proportions:

Acryloid AT-954	6,000.0 g	38.39%
Cymel 323	2,036.5 g	13.03%
pigment	6,000.0 g	38.39%
methyl amyl ketone	1,123.5 g	7.19%
acetone	455.0 g	2.91%
L7602 surfactant	14.0 g	0.09%
Total	15,629.0 g	100.00%

The acrylic polymer had the following molecular weight:

Molecular weight	6,070 weight average (Mw)
Molecular weight	1,670 number average (Mn)
Mw/Mn	3.63

The coating formulation contained 81.44% solids fraction and 18.56% solvent and surfactant fraction, with the following component composition:

AT-954 polymer	5,100.0 g	32.63%
Cymel 323 polymer	1,629.2 g	10.42%
pigment	6,000.0 g	38.39%
methyl amyl ketone	2,023.5 g	12.95%
acetone	455.0 g	2.91%
isobutanol	407.3 g	2.61%
L7602	14.0 g	0.09%
Total	15,629.0 g	100.00%

The solids fraction had the following composition:

AT-954 polymer	5,100.0 g	40.06%
Cymel 323 polymer	1,629.2 g	12.80%
pigment	6,000.0 g	47.14%
Total	12,729.2 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
acetone	455.0 g	15.77%	1440
isobutanol	407.3 g	14.11%	74
methyl amyl ketone	2,023.5 g	70.12%	40
Total	2,885.8 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	70%
50 to 100	14%
101 to 250	0%
ї 250	16%

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The coating formulation had the following properties:

Solvent content	259 grams/liter
Relative evap. rate	51 (butyl acetate = 100)
Viscosity	540 centipoise (23 C)
Weight solids	81.44 percent
Liquid density	1395 grams/liter

The spray mixture was prepared and sprayed in the continuous mode by admixing the coating formulation with the desired proportion of compressed carbon dioxide, both pressurized to the desired spray pressure. The spray mixture had a high compressed carbon dioxide content of 39% by weight and had the following composition:

Solids	50%
Carbon dioxide	39%
Organic Solvents	11%
Total	100%

Therefore, the spray mixture contained 3.5 times more compressed carbon dioxide than organic solvent.

The spray mixture was sprayed at an ambient temperature of 23 C with a spray pressure of 900 psi using a Nordson A7A automatic spray gun with Spraying Systems tip #400011, which has a 9-mil orifice size, a 40-degree spray angle rating, and a 7-inch fan width rating, with tip insert #15153-NY. At this temperature, compressed carbon dioxide has a

vapor pressure of 888 psi and has equilibrium gas and
liquid densities of 0.22 and 0.73 g/cc,
respectively. Therefore, the spray mixture contained
coating formulation admixed with compressed carbon
dioxide that was on the liquid side of equilibrium
conditions.

The spray was a feathered flat spray fan
that was parabolic in shape and that left the orifice
at a very large angle. The fan width was about 14
inches. Coatings were sprayed that had the following
properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.0 mil	70%	75%	44%
1.6 mil	74%	90%	72%
2.0 mil	73%	85%	63%
2.5 mil	78%	95%	82%
2.8 mil	75%	95%	83%
3.9 mil	71%	80%	50%

The pigmented coatings were uniformly white and had
very good appearance. They were very smooth with
high gloss and high distinctness of image. They were
free of haze and bubbles and even the very thick
coatings did not run or sag or have solvent popping.

Coatings were also sprayed at an ambient
temperature of 24 C with a spray pressure of 900
psi. At this temperature, the compressed carbon

dioxide has a vapor pressure of 908 psi and has
equilibrium gas and liquid densities of 0.23 and 0.72
g/cc, respectively. Therefore, the spray mixture
contained coating formulation admixed with compressed
carbon dioxide that was near the equilibrium
condition at which gas and liquid exist together.
The coatings had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.1 mil	73%	75%	48%
1.5 mil	75%	85%	61%
1.6 mil	80%	90%	71%
1.7 mil	78%	85%	65%
1.8 mil	79%	90%	72%
1.9 mil	79%	90%	79%
1.9 mil	79%	95%	81%
2.2 mil	78%	85%	63%
2.2 mil	79%	90%	73%
2.3 mil	78%	85%	65%
2.3 mil	78%	90%	73%
2.4 mil	79%	90%	80%
2.4 mil	78%	90%	78%
2.5 mil	80%	95%	82%
2.6 mil	79%	90%	77%
2.6 mil	79%	90%	74%

The pigmented coatings were uniformly white and had
very good appearance. They were very smooth with
high gloss and high distinctness of image. They were
free of haze and bubbles and did not run or sag or
have solvent popping.

Coatings were also sprayed at an ambient
temperature of 26 C with a spray pressure of 900
psi. At this temperature, the compressed carbon
dioxide has a vapor pressure of 950 psi and has
equilibrium gas and liquid densities of 0.25 and 0.69
g/cc, respectively. Therefore, the spray mixture
contained coating formulation admixed with compressed
carbon dioxide gas. The coatings had the following
properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.9 mil	70%	70%	39%
1.4 mil	77%	85%	63%
1.7 mil	77%	85%	69%
2.4 mil	80%	90%	72%

The pigmented coatings were uniformly white and had
very good appearance. They were very smooth with
high gloss and high distinctness of image. They were
free of haze and bubbles and did not run or sag or
have solvent popping.

Example 9

To see the effect of higher solids content
and higher viscosity on the spray, a sample of the
pigmented coating of Example 8 that did not contain
the acetone dilution was sprayed. The coating

formulation had a very high solids content or 83.89%
and a viscosity of 1060 centipoise (23 C). The
solids fraction was unchanged and the solvent
fraction had the following composition and relative
evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isobutanol	407.3 g	16.76%	74
methyl amyl ketone	2,023.5 g	83.24%	40
Total	2,430.8 g	100.00%	

The spray mixture was sprayed at an ambient
temperature of 26 C and a spray pressure of 900 psi.
At this temperature, the compressed carbon dioxide
has a vapor pressure of 950 psi and has equilibrium
gas and liquid densities of 0.25 and 0.69 g/cc,
respectively. Therefore, the spray mixture contained
coating formulation admixed with compressed carbon
dioxide gas. The carbon dioxide content was
increased from 28% up to 39%, and a feathered spray
was produced over the entire range. The spray was
fingered at the 28% concentration but became uniform
at 39% concentration, with the spray mixture having
the following composition:

Solids	51%
Carbon dioxide	39%
Solvents	10%
Total	100%

Therefore, the spray mixture contained four times more compressed carbon dioxide than organic solvent. No panels were sprayed.

Example 10

A coating formulation that has a solids content of 66.73% and a viscosity of 670 centipoise and that gives a clear acrylic coating was prepared from Rohm & Haas Acryloid[tm] AT-400 resin, which contains 75% nonvolatile acrylic polymer dissolved in 25% methyl amyl ketone solvent; Acryloid[tm] AT-954 resin; and Cymel[tm] 323 resin, by mixing the resins with solvents ethyl 3-ethoxypropionate (EEP), n-butanol, and methyl amyl ketone, and with 50% surfactant L7605 in xylene, in the following proportions:

Acryloid AT-400	8,150.6 g	50.04%
Acryloid AT-954	2,397.2 g	14.72%
Cymel 323	3,397.5 g	20.86%
EEP	1,111.3 g	6.82%
n-butanol	782.5 g	4.80%
methyl amyl ketone	400.0 g	2.46%
50% L5310 in xylene	48.8 g	0.30%
Total	16,287.9 g	100.00%

The acrylic polymers had the following molecular weights:

<u>Acryloid AT-400</u>

Molecular weight	9,280	weight average (Mw)
Molecular weight	3,270	number average (Mn)
Mw/Mn	2.84	

<u>Acryloid AT-954</u>

Molecular weight	6,070	weight average (Mw)
Molecular weight	1,670	number average (Mn)
Mw/Mn	3.63	

The coating forumulation contained 66.73% solids
fraction and 33.27% solvent and surfactant fraction,
with the following component composition:

AT-400 polymer	6,113.0 g	37.53%
AT-954 polymer	2,037.6 g	12.51%
Cymel 323 polymer	2,718.0 g	16.69%
methyl amyl ketone	2,797.2 g	17.18%
EEP	1,111.3 g	6.82%
n-butanol	782.5 g	4.80%
isobutanol	679.5 g	4.17%
xylene	24.4 g	0.15%
L5310	24.4 g	0.15%
Total	16,287.9 g	100.00%

The solids fraction had the following composition:

AT-400 polymer	6,113.0 g	56.24%
AT-954 polymer	2,037.6 g	18.75%
Cymel 323 polymer	2,718.0 g	25.01%
Total	10,868.6 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isobutanol	679.5 g	12.60%	74
xylene	24.4 g	0.45%	70
n-butanol	782.5 g	14.50%	44
methyl amyl ketone	2,797.2 g	51.85%	40
EEP	1,111.3 g	20.60%	11
Total	5,394.9 g	100.00%	

The coating formulation had the following properties:

Solvent content	336	grams/liter
Relative evap. rate	27	(butyl acetate = 100)
Viscosity	670	centipoise
Weight solids	66.73	percent
Liquid density	1013	grams/liter

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	87%
50 to 100	13%
101 to 250	0%
ï 250	0%

Spray mixtures were prepared and sprayed in
the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray

pressure. The spray mixtures were sprayed using a
Nordson A7A automatic spray gun with Binks tip
#9-0940, which has a 9-mil orifice size and a 7-inch
fan width rating, using Spraying Systems tip insert
#15153-NY. The distance from the spray tip to the
panel was eleven inches. Panels were sprayed using a
Spraymation automatic sprayer.

A spray mixture with a compressed carbon
dioxide content of 27.8% by weight at a temperature
of 26 C and pressure of 1600 psi produced a fishtail
spray pattern with atomization occurring from a
visible liquid-film that extended from the spray
orifice. The spray fan was angular in shape and had
a fan width of 7 inches. Spraying panels produced
liquid coatings that consisted of foam and baked
coatings that were covered with bubbles. The spray
viscosity was 23 centipoise as measured using a
Cambridge high- pressure viscometer.

Increasing the carbon dioxide concentration
to 28.5% and the temperature to 28 C and decreasing
the pressure to 1500 psi produced a wide feathered
flat spray fan that was parabolic in shape and that
left the orifice at a very large angle. The fan
width was about 11-12 inches. The spray had jetting
in the center of the fan that dissipated with
distance from the orifice. At this temperature,
compressed carbon dioxide has a vapor pressure of 995
psi and has equilibrium gas and liquid densities of
0.28 and 0.65 g/cc, respectively. Therefore, the
spray mixture contained coating formulation admixed

with liquid carbon dioxide, which was completely
dissolved. Coatings were sprayed that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.2 mil	79%	65%	30%
1.9 mil	88%	80%	50%
2.0 mil	90%	80%	49%

The coatings were smooth and glossy and free of haze
or bubbles.

Decreasing the pressure to 1200 psi gave a
feathered spray with little if any jetting. Coatings
were sprayed that had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.8 mil	84%	70%	39%
2.2 mil	89%	80%	49%

The coatings were smooth and glossy and free of haze
or bubbles.

Increasing the carbon dioxide concentration
to 29.6% and lowering the spray pressure to 1000 psi
at the temperature of 28 C gave a single-phase spray
mixture that was at or near the equilibrium condition
where carbon dioxide liquid and gas exist together.

The spray was feathered and uniform with no jetting.
Coatings were sprayed that had the following
properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.5 mil	73%	65%	28%
1.7 mil	83%	75%	42%
2.0 mil	86%	75%	45%
2.3 mil	88%	80%	52%
2.5 mil	90%	85%	59%

The coatings were smooth and glossy and free of haze
or bubbles.

Decreasing the pressure to 950 psi gave a
single-phase spray mixture that contained coating
formulation admixed with carbon dioxide gas, which
was completely dissolved. The spray viscosity was 19
centipoise as measured using a Cambridge
high-pressure viscometer. The spray was feathered
and uniform. Coatings were sprayed that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.0 mil	40%	---	---
1.1 mil	48%	---	---
1.7 mil	74%	---	---

1.9 mil	78%	70%	33%
2.1 mil	82%	70%	36%
2.2 mil	85%	75%	42%
2.7 mil	86%	80%	47%

The coatings were smooth and glossy and free of haze or bubbles.

Coatings were also sprayed at a temperature of 29 C and pressure of 900 psi, which was close to the carbon dioxide solubility limit. The coatings had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.8 mil	83%	70%	36%
1.1 mil	92%	80%	51%
1.4 mil	91%	80%	53%
1.8 mil	92%	85%	59%

The coatings were smooth and glossy and free of haze or bubbles.

For comparison, the coating formulation was sprayed without admixing it with compressed carbon dioxide. At a spray temperature of 28 C, from the lowest to the highest spray pressure used (1600 psi) the spray had a fishtail spray pattern with atomization occurring from a visible liquid-film that extended from the spray orifice. The spray fan was angular in shape and had side jets detached from the

central portion of the spray. The spray deposition
pattern was very nonuniform and the liquid coatings
sprayed were foamy from air entrapment. The baked
coatings were covered with air bubbles.

For comparison, the coating formulation was
also sprayed without admixing it with compressed
carbon dioxide but admixing it with methyl ethyl
ketone solvent, which has a very high relative
evaporation rate, to a concentration of 28% by weight
in order to reduce the viscosity to a low level.
Over all the ranges of spray temperature (23-60 C)
and pressure (300-1600 psi) examined, the spray had a
fishtail spray pattern with atomization occurring
from a visible liquid-film that extended from the
spray orifice. The spray fan was angular in shape
and had side jets detached from the central portion
of the spray. The spray deposition pattern was
nonuniform and the coatings were poor.

Example 11

The coating formulation used in Example 10
was sprayed using the same spray gun and tip but at
an ambient temperature of 21 C. At this temperature,
compressed carbon dioxide has a vapor pressure of 846
psi and has equilibrium gas and liquid densities of
0.20 and 0.76 g/cc, respectively. Therefore, the
spray mixtures contained coating formulation admixed
with liquid carbon dioxide.

With a carbon dioxide concentration of about
28.2%, at spray pressures of 1000 and 1600 psi, the
spray mixture was a clear single-phase solution and
produced a fishtail spray pattern with atomization
occurring from a visible liquid-film that extended
from the spray orifice. The spray fan was angular in
shape and and had a fan width of - inches. Spraying
panels produced liquid coatings that were foam and
baked coatings that were covered with clusters of
foam bubbles. The spray viscosity was 23 centipoise
as measured using a Cambridge high-pressure
viscometer.

A carbon dioxide concentration of 31.5% gave
a two-phase mixture at a spray pressure of 1600 psi,
which indicates that liquid carbon dioxide in excess
of the solubility limit was dispersed as fine
droplets in the spray mixture. The spray was in
transition between a fishtail and a feathered spray,
being flared outward on both sides from the plane of
the fan and therefore not being a flat fan. Coatings
were sprayed that were clear, smooth, and glossy and
that were free of haze and bubbles. They had the
following properties:

Coating Thickness	20-Degree Gloss
0.6 mil	32%
1.2 mil	60%
1.3 mil	68%
1.6 mil	63%

Lowering the pressure increased the width of the spray and decreased the amount of flaring.

Increasing the carbon dioxide concentration to 36.0% gave a spray mixture that had two phases even at a high pressure of 2000 psi, which indicates that a substantial excess of liquid carbon dioxide above the solubility limit was dispersed as fine droplets in the spray mixture at lower pressures. At 2000 psi, the spray mixture produced a feathered spray with a parabolic shape, but the high pressure produced jetting in the center, which dissipated with greater distance from the orifice. A coating was sprayed with a thickness of 1.3 mil and a gloss of 74%. It was clear, smooth, and glossy and was free of haze and bubbles.

Decreasing the pressure to 1550 psi decreased the amount of jetting in the spray. A coating was sprayed with a thickness of 1.0 mil and a gloss of 65% and that was free of haze and bubbles. Decreasing the pressure to 900 psi gave a feathered spray with no jetting and a wider fan. A coating was sprayed in the same manner as at the higher pressures and it had a thickness of 0.5 mil, which indicates a much lower spray rate.

Example 12

A coating formulation that has a solids content of 64.32% and a viscosity of 540 centipoise (23 C) and that gives a clear acrylic coating was prepared from Acryloid^{tm} AT-400 resin, Acryloid^{tm} AT-954 resin, and Cymel^{tm} 323 resin, by mixing the resins with solvents ethyl 3-ethoxypropionate (EEP), n-butanol, acetone, and methyl amyl ketone, and with 50% surfactant L7605 in xylene, in the following proportions:

Acryloid AT-400	8,150.6 g	48.23%
Acryloid AT-954	2,397.2 g	14.19%
Cymel 323	3,397.5 g	20.10%
EEP	1,111.3 g	6.58%
n-butanol	782.5 g	4.63%
acetone	612.1 g	3.62%
methyl amyl ketone	400.0 g	2.37%
50% L5310 in xylene	48.8 g	0.29%
Total	16,900.0 g	100.00%

The acrylic polymers had the following molecular weights:

Acryloid AT-400

Molecular weight	9,280 weight average (Mw)
Molecular weight	3,270 number average (Mn)
Mw/Mn	2.84

<u>Acryloid AT-954</u>

Molecular weight   6,070 weight average (Mw)
Molecular weight   1,670 number average (Mn)
Mw/Mn   3.63

The coating formulation contained 64.32% solids
fraction and 35.68% solvent and surfactant fraction,
with the following component composition:

AT-400 polymer	6,113.0 g	36.17%
AT-954 polymer	2,037.6 g	12.06%
Cymel 323 polymer	2,718.0 g	16.09%
methyl amyl ketone	2,797.2 g	16.55%
EEP	1,111.3 g	6.58%
n-butanol	782.5 g	4.63%
isobutanol	679.5 g	4.02%
acetone	612.1 g	3.62%
xylene	24.4 g	0.14%
L5310	24.4 g	0.14%
Total	16,900.0 g	100.00%

The solids fraction had the following composition:

AT-400 polymer	6,113.0 g	56.24%
AT-954 polymer	2,037.6 g	18.75%
Cymel 323 polymer	2,718.0 g	25.01%
Total	10,868.6 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
acetone	612.1 g	10.19%	1440
isobutanol	679.5 g	11.31%	74
xylene	24.4 g	0.40%	70
n-butanol	782.5 g	13.03%	44
methyl amyl ketone	2,797.2 g	46.57%	40
EEP	1,111.3 g	18.50%	11
Total	6,007.0 g	100.00%	

The coating formulation had the following properties:

Solvent content	357	grams/liter
Relative evap. rate	27	(butyl acetate = 100)
Viscosity	540	centipoise
Weight solids	64.32	percent
Liquid density	1001	grams/liter

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	78%
50 to 100	12%
101 to 250	0%
ï 250	10%

Spray mixtures were prepared and sprayed in
the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. The spray mixtures were sprayed using a
Nordson A7A automatic spray gun with Spraying Systems

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tip #400011, which has a 9-mil orifice size and a
7-inch fan width rating, using tip insert #15153-NY.
The distance from the spray tip to the panel was
twelve inches. Panels were sprayed using a
Spraymation automatic sprayer.

The spray mixture had a compressed carbon
dioxide content of 32.5% by weight and was sprayed at
a temperature of 28 C and a pressure of 900 psi. At
this temperature, compressed carbon dioxide has a
vapor pressure of 995 psi and has equilibrium gas and
liquid densities of 0.28 and 0.65 g/cc,
respectively. Therefore, the spray mixture contained
coating formulation admixed with compressed carbon
dioxide gas. The spray mixture was close to the
carbon dioxide solubility limit at these conditions.
The spray was a feathered flat spray fan that was
parabolic in shape and that left the orifice at a
very large angle. The fan width was about 14
inches. Coatings were sprayed that had the following
properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.7 mil	69%	65%	30%
1.0 mil	86%	70%	38%
1.3 mil	88%	80%	52%

The coatings were smooth and glossy and free of haze
or bubbles.

Example 13

A pigmented coating formulation that has a solids content of 70.76% and a viscosity of 1200 centipoise (23 C) and that gives a white acrylic coating was prepared from Acryloid[tm] AT-400 resin and Cymel[tm] 323 resin by mixing the resins with Dupont Ti-pure[tm] 960 titanium dioxide pigment and with solvents n-butanol and methyl amyl ketone, in the following proportions:

Acryloid AT-400	6,000.0 g	38.86%
Cymel 323	1,883.7 g	12.20%
pigment	4,917.6 g	31.85%
n-butanol	1,426.7 g	9.24%
methyl amyl ketone	1,212.0 g	7.85%
Total	15,440.0 g	100.00%

The acrylic polymer had the following molecular weight:

Molecular weight	9,280 weight average (Mw)
Molecular weight	3,270 number average (Mn)
Mw/Mn	2.84

The coating formulation contained 70.76% solids fraction and
29.24% solvent fraction, with the following component composition:

AT-400 polymer	4,500.0 g	29.15%
Cymel 323 polymer	1,507.0 g	9.76%
pigment	4,917.6 g	31.85%
methyl amyl ketone	2,712.0 g	17.56%
n-butanol	1,426.7 g	9.24%
isobutanol	376.7 g	2.44%
Total	15,440.0 g	100.00%

The solids fraction had the following composition:

AT-400 polymer	4,500.0 g	41.19%
Cymel 323 polymer	1,507.0 g	13.80%
pigment	4,917.6 g	45.01%
Total	10,924.6 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isobutanol	376.7 g	8.34%	74
n-butanol	1,426.7 g	31.60%	44
methyl amyl ketone	2,712.0 g	60.06%	40
Total	4,515.4 g	100.00%	

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	92%
50 to 100	8%
101 to 250	0%
ï 250	0%

The coating formulation had the following properties:

Solvent content   376 grams/liter
Relative evap. rate   43 (butyl acetate = 100)
Viscosity   1,200 centipoise (23 C)
Weight solids   70.76 percent
Liquid density   1286 grams/liter

The spray mixture was prepared and sprayed
in the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. The spray mixture had a compressed carbon
dioxide content of 32% by weight and had the
following composition:

Solids   48%
Carbon dioxide   32%
Organic Solvents   20%
Total   100%

Therefore, the spray mixture contained 60% more
compressed carbon dioxide than organic solvent.

The spray mixture was sprayed at an ambient
temperature of 23.4 C and a spray pressure of 900 psi
using a Nordson A7A automatic spray gun with
Spraying Systems tip #400011, which has a 9-mil
orifice size and a 7-inch fan width rating, with tip
insert #15153-NY. At this temperature, compressed
carbon dioxide has a vapor pressure of 896 psi and

has equilibrium gas and liquid densities of 0.22 and
0.73 g/cc, respectively. Therefore, the spray
mixture contained coating formulation admixed with
compressed carbon dioxide that was at or near the
equilibrium
condition where carbon dioxide gas and liquid exist
together.

    The spray mixture produced a feathered flat
spray fan that was parabolic in shape and that left
the orifice at a very large angle. The fan width was
about 7-9 inches. Coatings were sprayed that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.9 mil	63%	80%	46%
1.5 mil	67%	80%	48%

The pigmented coatings were smooth and white in
appearance. They were free of bubbles and did not
run or sag.

    A Nordson flat spray tip #016-013, which has
a 9-mil orifice size and a 6-inch fan width rating,
was used with turbulence plate #029-012. This
produced a narrower feathered spray fan with a width
of about 6-7 inches. A coating was sprayed that had
a thickness of 1.7 mil and a gloss of 64%.

The spray mixture was also sprayed at an
ambient temperature of 26.7 C and a spray pressure of
900 psi using the same Nordson A7A spray gun and
Spraying Systems tip #400011. At this temperature,
compressed carbon dioxide has a gas pressure of 966
psi and has equilibrium gas and liquid densities of
0.26 and 0.68 g/cc, respectively. Therefore, the
spray mixture contained coating formulation admixed
with compressed carbon dioxide gas.

The spray mixture produced a feathered flat
spray fan that was parabolic in shape and that left
the orifice at a very large angle. The fan width was
about 7-9 inches. Coatings were sprayed that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.5 mil	50%	---	---
0.9 mil	64%	75%	44%
1.2 mil	62%	75%	42%
1.3 mil	75%	75%	43%
1.6 mil	63%	75%	40%

Increasing the spray pressure to 1200 psi produced a
feathered spray that was narrower and the had some
jetting in the center, which dissipated with
distance. A coating was sprayed that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
1.5 mil	70%	85%	55%

The pigmented coatings were smooth, glossy, and white in appearance. They were free of bubbles and did not run or sag.

Reducing the carbon dioxide concentration to below 28% by weight produced a fishtail spray that was angular in shape. This produced liquid coatings that were foamed and baked coatings that were covered with bubbles.

Example 14

A coating formulation that has a solids content of 60.00% and a viscosity of 470 centipoise (23 C) and that gives a clear acrylic coating was prepared by mixing Acryloid^{tm} AT-400 resin and Cymel^{tm} 323 resin with solvents methyl amyl ketone and n-butanol in the following proportions:

Acryloid AT-400	8,694.0 g	60.00%
Cymel 323	2,718.0 g	18.75%
methyl amyl ketone	2,453.0 g	16.93%
n-butanol	626.0 g	4.32%
Total	14,491.0 g	100.00%

The acrylic polymer had the following molecular
weight:

Molecular weight	9,280 weight average (Mw)	
Molecular weight	3,270 number average (Mn)	
Mw/Mn	2.84	

The coating formulation had the following component
composition:

AT-400 polymer	6,520.5 g	45.00%
Cymel 323 polymer	2,174.4 g	15.00%
methyl amyl ketone	4,626.5 g	31.93%
n-butanol	626.0 g	4.32%
isobutanol	543.6 g	3.75%
Total	14,491.0 g	100.00%

The coating formulation had a solvent content of 394
grams/liter.

        The spray mixture was prepared and sprayed
in the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. It was sprayed using a Nordson A7A
automatic spray gun with Binks tip #9-0940, which has
a 9-mil orifice size and a 7-inch fan width rating,
using Spraying Systems tip insert #15153-NY.

        The spray mixture had a compressed carbon
dioxide content of 28.2% by weight and was sprayed at
a pressure of 950 psi at various temperatures to

observe the change in the spray pattern. At a vapor
pressure of 950 psi, compressed carbon dioxide has an
equilibrium temperature of 26 C and has equilibrium
gas and liquid densities of 0.25 and 0.69 g/cc,
respectively. Therefore, the spray mixture contained
coating formulation admixed with carbon dioxide
liquid below this temperature and with gas above this
temperature.

At the ambient temperature of 24 C, the
spray was in transition between a fishtail and a
feathered spray. It remained in transition up to a
temperature of 36 C, which produced a wide uniform
flat feathered spray with a parabolic shape. The fan
width was about 12 inches.

Example 15

A coating formulation that has a solids
content of 55.00% and a low viscosity of 220
centipoise (23 C) and that gives a clear acrylic
coating was prepared by mixing Acryloid^{tm} AT-400
resin and Cymel^{tm} 323 resin with solvents methyl amyl
ketone and n-butanol in the following proportions:

Acryloid AT-400	8,694.0 g	55.00%
Cymel 323	2,718.0 g	17.19%
methyl amyl ketone	3,771.0 g	23.85%
n-butanol	626.0 g	3.96%
Total	15,809.0 g	100.00%

The acrylic polymer had the following molecular
weight:

Molecular weight	9,280 weight average (Mw)
Molecular weight	3,270 number average (Mn)
Mw/Mn	2.84

The coating formulation had the following component
composition:

AT-400 polymer	6,520.5 g	41.25%
Cymel 323 polymer	2,174.4 g	13.75%
methyl amyl ketone	5,944.5 g	37.60%
n-butanol	626.0 g	3.96%
isobutanol	543.6 g	3.44%
Total	15,809.0 g	100.00%

The coating formulation had a solvent content of 436
grams/liter.

The spray mixture was prepared and sprayed
in the continuous mode by admixing the coating
formulation with the desired proportion of compressed
carbon dioxide, both pressurized to the desired spray
pressure. It was sprayed using a Nordson A7A
automatic spray gun with Binks tip #9-0940, which has
a 9-mil orifice size and a 7-inch fan width rating,
using Spraying Systems tip insert #15153-NY.

The spray mixture had a compressed carbon
dioxide content of 28.2% by weight and was sprayed at

a pressure of 950 psi at various temperatures to
observe the change in the spray pattern. At a vapor
pressure of 950 psi, compressed carbon dioxide has an
equilibrium temperature of 26 C and has equilibrium
gas and liquid densities of 0.25 and 0.69 g/cc,
respectively. Therefore, the spray mixture contained
coating formulation admixed with carbon dioxide
liquid below this temperature and with gas above this
temperature.

At the ambient temperature of 24 C, the
spray was in transition between a fishtail and a
feathered spray. It remained in transition up to a
temperature of 36 C, which produced a wide uniform
flat feathered spray with a parabolic shape. The fan
width was about 12 inches.

To see the effect of lower pressure on the
change in the spray with temperature, the spray
mixture was sprayed at a pressure of 800 psi. The
ambient temperature of 25.7 C produced a wide uniform
flat feathered spray with a parabolic shape. At this
temperature, compressed carbon dioxide has a vapor
pressure of 945 psi and equilibrium gas and liquid
densities of 0.25 and 0.69 g/cc, respectively.
Therefore, the spray mixture contained coating
formulation admixed with carbon dioxide gas, which
was completely dissolved. The spray mixture was then
sprayed using Nordson flat spray tip #016-013, which
has a 9-mil orifice size and a 6-inch fan width
rating, using turbulence plate #029-?12. This·
produced a narrow feathered spray fan with a

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parabolic shape and a width of about 6-7 inches. The
spray mixture was then sprayed using Graco fine
finish tip #163-416, which has a large 16-mil orifice
size and a 9-inch fan width rating. This produced a
very wide feathered spray fan with a parabolic shape
and a width of about 14-16 inches.

Example 16

A coating formulation that has a solids
content of 65.01% and a viscosity of 940 centipoise
and that gives a clear acrylic coating was prepared
from by mixing Acryloid^{tm} AT-400 resin and Cymel^{tm}
323 resin witn solvents methyl amyl ketone and
n-butanol in the following proportions:

Acryloid AT-400	8,694.0 g	65.01%
Cymel 323	2,718.0 g	20.32%
methyl amyl ketone	1,336.0 g	9.99%
n-butanol	626.0 g	4.68%
Total	13,374.0 g	100.00%

The acrylic polymer had the following molecular
weight:

Molecular weight	9,280 weight average (Mw)
Molecular weight	3,270 number average (Mn)
Mw/Mn	2.84

The coating formulation had the following component
composition:

AT-400 polymer	6,520.5 g	48.75%
Cymel[tm] 323 polymer	2,174.4 g	16.26%
isobutanol	543.6 g	4.07%
n-butanol	626.0 g	4.68%
methyl amyl ketone	3,509.5 g	26.24%
Total	13,374.0 g	100.00%

The coating formulation had a solvent content of 394 grams/liter.

The coating formulation was admixed with subcritical compressed carbon dioxide at different concentrations and sprayed at different temperatures and pressures. All the subcritical spray conditions tried produced a fishtail liquid-film spray. A feathered decompressive spray could not be obtained at this high solids content.

Example 17

A coating formulation that has a solids content of 69.43% and a viscosity of 1080 centipoise (23 C) and that gives a clear air-dry alkyd-urea catalzyed conversion coating was prepared from a special Reichhold alkyd resin, which contains 75% alkyd polymer in 25% methyl amyl ketone solvent, and American Cyanamid Beetle[tm] 80 resin, which is an acid catalyzed cross-linking agent that contains 96% butylated urea-formaldehyde polymer and 4% n-butanol, by mixing the resins with solvents

n-butanol and Aromatic 100 and with Union Carbide surfactant SILWET^{tm} L-7500, in the following proportions:

Reichhold alkyd	10,000.0 g	66.20%
Beetle 80	3,111.8 g	20.60%
n-butanol	1,057.4 g	7.00%
Aromatic 100	906.3 g	6.00%
SILWET L-7500	30.2 g	0.20%
Total	15,105.7 g	100.00%

The alkyd polymer had the following molecular weight:

Molecular weight	15,830 weight average (Mw)
Molecular weight	1,980 number average (Mn)
Mw/Mn	8.00

The coating formulation contained 69.43% solids fraction and 30.57% solvent and surfactant fraction, with the following component composition:

Reichhold alkyd	7,500.0 g	49.65%
Beetle 80	2,987.3 g	19.78%
methyl amyl ketone	2,500.0 g	16.55%
n-butanol	1,181.9 g	7.82%
Aromatic 100	906.3 g	6.00%
SILWET L-7500	30.2 g	0.20%
Total	15,105.7 g	100.00%

The solids fraction had the following composition:

Reichhold alkyd	7,500.0 g	71.52%
Beetle 80	2,987.3 g	28.48%
Total	10,487.3 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
n-butanol	1,181.9 g	25.76%	44
methyl amyl ketone	2,500.0 g	54.49%	40
Aromatic 100	906.3 g	19.75%	20
Total	4,588.2 g	100.00%	

The coating formulation had the following properties:

Property	
Solvent content	304 grams/liter
	2.54 lb/gal]
Relative evap. rate	34 (butyl acetate = 100)
Viscosity	1080 centipoise
Weight solids	69.43 percent
Liquid density	996 grams/liter

The solvent fraction had the following distribution
of solvent by relative evaporation rate:

< 50	100%
50 to 100	0%
101 to 250	0%
ï 250	0%

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Prior to spraying, 0.4% of American Cyanamid
Cycat^{tm} 4040 catalyst was admixed with the coating
formulation to initiate the crosslinking reaction.
The spray mixture was prepared and sprayed in the
continuous mode by admixing the coating formulation
with the desired proportion of compressed carbon
dioxide, both pressurized to the desired spray
pressure. The spray mixture was sprayed using a
Nordson A7A automatic spray gun with Binks tip
#400011, which has a 9-mil orifice size and a 7-inch
fan width rating, using tip insert #15153-NY. The
distance from the spray tip to the panel was twelve
inches. Panels were sprayed using a Spraymation
automatic sprayer.

The spray mixture had a compressed carbon
dioxide content of 30% by weight and was sprayed at
the ambient temperature of 25.8 C and a pressure of
900 psi. At this temperature, compressed carbon
dioxide has a vapor pressure of 947 psi and has
equilibrium gas and liquid densities of 0.25 and 0.69
g/cc, respectively. Therefore, the spray mixture
contained coating formulation admixed with compressed
carbon dioxide gas, which was completely dissolved.
The spray was a feathered flat spray fan that was
parabolic in shape and that left the orifice at a
very large angle. The fan width was about 11-12
inches. After waiting about two hours, coatings were
sprayed over a period of one half hour that had the
following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.7 mil	71%	65%	28%
1.0 mil	85%	70%	37%
1.2 mil	83%	70%	34%
1.5 mil	91%	80%	46%

The coatings were smooth, glossy, and had good appearance. They were free of haze or bubbles.

Not long after the coatings were sprayed, the viscosity of the coating formulation was measured and was found to have increased from 1080 centipoise, when the catalyst was added, to 1800 centipoise, due to the catalyzed cross-linking reaction increasing the molecular weight of the polymer system, which had caused the spray to begin to deteriorate. The coating formulation was then diluted with acetone to a viscosity of 500 centipoise and spraying was continued at a pressure of 850 psi. Coatings were sprayed that had the following properties:

Coating Thickness	20-Degree Gloss	MDEC DOI	ATI DOI
0.6 mil	60%	---	---
			12N47-06 Center
1.0 mil	80%	70%	36%

12N47-09

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1.0 mil	87%	70%	37%
12N47-07 Center			
1.5 mil	90%	80%	45%
12N47-08 Center			

The coatings were smooth, glossy, and had good
appearance. They were free of haze or bubbles.
Shortly thereafter, the continued increase in
molecular weight of the coating formulation due to
the catalyzed reaction caused to the feathered spray
to deteriorate and eventually transition to an
angular fishtail spray pattern with atomization
occurring from a liquid-film that extended from the
spray orifice.

Example 18

A coating formulation that has a solids
content of 100% and a viscosity of 375 centipoise (23
C) and that gives a clear liquid coating used for
mold release applications such as in casting metal
items was the liquid silicone polymer
polydimethylsiloxane (Specialty Systems, Rochester
Hills, Michigan). The polymer had an estimated
weight-average molecular weight of between about 1000
and 2000.

A spray mixture was prepared by admixing the
liquid polymer with compressed carbon dioxide at a
concentration of about 30%. The spray mixture was
sprayed at a temperature of 21 C and a pressure of

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825 psi. This produced a uniform angular spray fan
with liquid-film type atomization and a width of
about 8 inches at a distance of 12 inches from the
spray tip. Although angular in shape, the spray
produced relatively uniform coating deposition and a
liquid coating having a thickness of about 2 mil that
was free of bubbles and holes in the coating film and
were suitable for mold release applications.

     The compressed carbon dioxide concentration
in the spray mixture was then increased to about 40%
at a temperature of 21 C and a pressure of 800 psi.
This caused the spray to enter into transition
between the angular spray pattern and a feathered
parabolic spray pattern. The compressed carbon
dioxide concentration was then increased to about
50%. This produced a wide uniform feathered
decompressive spray pattern having a fan width of
about 12-14 inches. The spray produced uniform thin
liquid coatings having thicknesses from less than one
mil to greater than two mil that were free of bubbles
and holes in the coating film and were suitable for
mold release applications.

                    Example 19

     A coating formulation that has a solids
content of 55.00% and a viscosity of 1870 centipoise
and that gives a clear air-dry alkyd-urea
nitrocellulose lacquer coating was prepared from
Hercules grade R5-18-25 nitrocellulose, which

contains 70% solid nitrocellulose powder wetted with
30% isopropanol solvent, and Reichhold Beckosol[tm]
alkyd resin solution CO9195-02, which contains 75%
non-volatile short coconut oil alkyd in 25% methyl
amyl ketone solvent, by mixing the solid polymer and
resin solution with solvents methyl amyl ketone,
n-butanol, and dioctyl phthalate and with surfactant
SILWET[tm] L-7500, in the following proportions:

Nitrocellulose	3,825.0 g	25.50%
Reichhold alkyd	4,425.0 g	29.50%
methyl amyl ketone	4,785.0 g	31.90%
n-butanol	1,260.0 g	8.40%
dioctyl phthalate	690.0 g	4.60%
SILWET L-7500	15.0 g	0.10%
Total	15,000.0 g	100.00%

The nitrocellulose and alkyd polymers had the
following molecular weight:

Nitrocellulose

Molecular weight	25,725	weight average (Mw)
Molecular weight	9,760	number average (Mn)
Mw/Mn	2.64	

Alkyd polymer

Molecular weight	19,040	weight average (Mw)
Molecular weight	2,050	number average (Mn)
Mw/Mn	9.29	

The coating formulation contained 55.00% solids
fraction and 45.00% solvent and surfactant fraction,

with the following component composition:

Nitrocellulose	2,677.5 g	17.85%
Reichhold alkyd	3,318.8 g	22.12%
methyl amyl ketone	5,891.2 g	39.28%
isopropanol	1,147.5 g	7.65%
n-butanol	1,260.0 g	8.40%
dioctyl phthalate	690.0 g	4.60%
SILWET L-7500	15.0 g	0.10%
Total	15,000.0 g	100.00%

The solids fraction had the following composition:

Nitrocellulose	2,677.5 g	44.65%
Reichhold alkyd	3,318.8 g	55.35%
Total	5,996.3 g	100.00%

The solvent fraction had the following composition
and relative evaporation rates (butyl acetate = 100):

Solvent	Grams	Wt. %	RER
isopropanol	1,147.5 g	12.76%	288
n-butanol	1,260.0 g	14.02%	44
methyl amyl ketone	5,891.2 g	65.54%	40
dioctyl phthalate	690.0 g	7.68%	<1
Total	8,988.7 g	100.00%	

The coating formulation had the following properties:

Solvent content	443 grams/liter
Relative evap. rate	<10 (butyl acetate = 100)
Viscosity	1080 centipoise
Weight solids	55.00 percent
Liquid density	984 grams/liter

The solvent fraction had the following distribution of solvent by relative evaporation rate:

< 50	87%
50 to 100	0%
101 to 250	0%
ï 250	13%

The spray mixture was prepared and sprayed in the continuous mode by admixing the coating formulation with the desired proportion of compressed carbon dioxide, both pressurized to the desired spray pressure. The spray mixture was sprayed using a Nordson Model SCF-Ml hand spray gun with tip #0410, which has a 9-mil orifice size and a 10-12 inch fan width rating.

The spray mixture had a compressed carbon dioxide content of about 28% by weight and was sprayed at the ambient temperature of about 25 C and a pressure of 950 psi. This produced a narrow fishtail spray with a lengthy liquid film, which produced coatings full of bubbles. The coating composition was then thinned with methyl amyl ketone solvent to a viscosity of 1000 centipoise, but a fishtail liquid-film spray was still produced, which

increasing the carbon dioxide concentration did not
change. The coating composition was further thinned
with acetone to a viscosity of 500 centipoise and the
carbon dioxide concentration was increased first to
36% and then to higher concentrations. This failed
to achieve transition from the fishtail liquid-film
spray to a feathered spray. The coatings continued
to be full of bubbles because of the poor
atomization. Heating the spray mixture, lowering the
pressure, and using different spray nozzles,
including a turbulence promoter, failed to bring
about the transition or give coatings that were not
full of bubbles. This demonstrated that the
number-average molecular weight of the coating
composition was too high for spraying with
subcritical compressed carbon dioxide.

What is Claimed is:

1.   A process for reducing the viscosity of a
composition containing one or more liquid polymeric
compounds to make it transportable comprising forming
a liquid mixture in a closed system comprising:

        a)   a composition containing a first set of
at least one or more liquid polymeric compounds
wherein the number-average molecular weight (M_n) of
the one or more liquid polymeric compounds is less
than about 5,000; and

        b)   at least one subcritical compressed
fluid in at least an amount which when added to (a)
is sufficient to render the viscosity of said mixture
to a point suitable for being transportable, wherein
the subcritical compressed fluid is a gas at standard
conditions of $0^{\circ}C$ and one atmosphere (STP).

2.   The process of Claim 1, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
3,500.

3.   The process of Claim 2, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
2,500.

4.   The process of Claim 1, wherein a second set
of one or more polymeric compounds are contained in
the composition wherein at least 75% by weight of the
first and second sets of polymeric compounds in the
composition have a weight average molecular weight

(M_w) less than about 20,000 based on the combined
weight of the first set of the at least one or more
liquid polymeric compounds and the second set of the
at least one or more polymeric compounds.

5.   The process of Claim 4, wherein at least 80%
by weight of the first and second sets of polymeric
compounds in the composition have a weight average
molecular weight (M_w) less than about 15,000 based on
the combined weight of the first set of the at least
one or more liquid polymeric compounds and the second
set of the at least one or more polymeric compounds.

6.   The process of Claim 4, wherein at least 85%
by weight of the first and second sets of polymeric
compounds in the composition have a weight average
molecular weight (M_w) less than about 10,000 based on
the combined weight of the first set of the at least
one or more liquid polymeric compounds and the second
set of the at least one or more polymeric compounds.

7.   The process of Claim 1, wherein the
composition (a) has a solubility with the at least
one subcritical compressed fluid of at least about
10% by weight of the subcritical compressed fluid in
the liquid mixture formed.

8.   The process of Claim 7, wherein the
solubility is at least about 15% by weight of the
subcritical compressed fluid in the liquid mixture
formed.

9.   The process of Claim 7, wherein the
solubility is in the range of from about 20 to about
70% by weight of the subcritical compressed fluid in
the liquid mixture formed.

10.   The process of Claim 1, wherein the
viscosity of the mixture of (a) and (b) is less than
about 150 cps.

11.   The process of Claim 1, wherein the
viscosity of the mixture of (a) and (b) is less than
about 100 cps.

12.   The process of Claim 11, wherein the
viscosity of the mixture of (a) and (b) is in the
range of from about 1 to about 75 cps.

13.   The process of Claim 1 further comprising
adding to said liquid mixture at least one active
solvent (c) in which said at least one or more
polymeric compounds (a) are at least partially
soluble and which is at least partially miscible with
the subcritical compressed fluid (b), said solvent
being present in an amount such that the viscosity of
(a) and (c) is greater than about 150 cps but less
than about 4,000 cps.

14.   The process of Claim 13, wherein the
viscosity of the mixture of (a) and (c) is less than
about 2,000 cps.

15.   The process of Claims 1 or 13, wherein the
at least one subcritical compressed fluid comprises
carbon dioxide.

16.   The process of Claim 15, wherein the at
least one subcritical compressed fluid comprises
nitrous oxide.

17.   The process of Claim 15, wherein the at
least one subcritical compressed fluid comprises a
mixuture of carbon dioxide and nitrous oxide.

18.   The process of Claim 13, wherein the
viscosity of the mixture of (a), (b) and (c) is less
than about 150 cps.

19.   The process of Claim 18, wherein the
viscosity of the mixture of (a), (b) and (c) is less
than about 100 cps.

20.   The process of Claim 18, wherein the
viscosity of the mixture of (a), (b) and (c) is in
the range of from about 1 to about 75 cps.

21.   The process of Claim 1, wherein the liquid
mixture is formed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is greater than about 0.1.

22.   The process of Claim 21, wherein the liquid
mixture is formed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is greater than about 0.25.

23.   The process of Claim 1, wherein the liquid
mixture is formed at temperatures such that the

subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.8 when the
pressure is greater than the critical pressure of the
subcritical compressed fluid.

24.   The process of Claim 23, wherein the liquid
mixture is formed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.6 when the
pressure is greater than the critical pressure of the
subcritical compressed fluid.

25.   The process of Claim 1, wherein the liquid
mixture is formed at temperatures which are less than
about 20 degrees C above the critical temperature of
the subcritical compressed fluid when the pressure is
less than the critical pressure of the subcritical
compressed fluid.

26.   The process of Claim 25, wherein the liquid
mixture is formed at temperatures which are less than
about 10 degrees C above the critical temperature of
the subcritical compressed fluid when the pressure is
less than the critical pressure of the subcritical
compressed fluid.

27.   The process of Claim 1, wherein the liquid
mixture is formed at ambient temperature.

28.   The process of Claim 1, wherein the liquid
mixture is formed at a pressure less than about 95%
of the absolute critical pressure of the subcritical

compressed fluid when the temperature is above the critical temperature of the subcritical compressed fluid.

29.   The process of Claim 28, wherein the liquid mixture is formed at a pressure in the range of from about 50 to about 90% of the absolute critical pressure of the subcritical compressed fluid when the temperature is above the critical temperature of the subcritical compressed fluid.

30.   The process of Claim 1, wherein the liquid mixture is formed at a pressure less than about 600 psi above the critical pressure of the subcritical compressed fluid when the temperature is less than the critical temperature of the subcritical compressed fluid.

31.   The process of Claim 1, wherein the liquid mixture is formed at a pressure in the range of from about 500 to about 1020 psi when the subcritical compressed fluid is carbon dioxide.

33.   The process of Claim 31, wherein the liquid mixture is formed at a pressure in the range of from about 700 to about 970 psi when the subcritical compressed fluid is carbon dioxide.

34.   The process of Claim 1, wherein said one or more polymeric compounds are selected from the group consisting of acrylics, polyesters, melamines, alkyds, epoxies urethanes, urea formaldehydes, vinyls, silicone polymers and mixtures thereof.

35.   The process of Claim 13, wherein the at
least one active solvent is selected from the group
consisting of aliphatic or aromatic hydrocarbons,
ketones, esters, ethers, alcohols and mixtures
thereof.

36.   The process of Claim 35, wherein the active
solvent is a glycol ether.

37.   The process of Claim 1, wherein the liquid
mixture includes an additive selected from the group
consisting of pigments, drying agents, anti-skinning
agents, and combinations thereof.

38.   The process of Claim 1, wherein at least one
of the one or more polymeric compounds is a silicon
containing polymer.

39.   The process of Claim 1, wherein the at least
one of the one or more polymeric compounds is a
fluorine containing polymer.

40.   A process for reducing the viscosity of a
composition containing one or more polymeric
compounds to make it transportable comprising forming
a liquid mixture in a closed system comprising:
       a)   a composition containing a first set of
at least one or more polymeric compounds wherein the
number average molecular weight (M_n) of the one or
more polymeric compounds is less than about 5,000;
       b)   at least one subcritical compressed
fluid in at least an amount which when added to (a)
and (c) is sufficient to render the viscosity of said
mixture to a point suitable for being transportable,

wherein the subcritical compressed fluid is a gas at
standard conditions of $0^\circ C$ and one atmosphere (STP);
and

c)   at least one active solvent in which
said one or more polymeric compounds are at least
partially soluble and which is at least partially
miscible with the subcritical compressed fluid.

41.   The process of Claim 40, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
3,500.

42.   The process of Claim 41, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
2,500.

43.   The process of Claim 40, wherein a second
set of one or more polymeric compounds are contained
in the composition wherein at least 75% by weight of
the first and second sets of polymeric compounds in
the composition have a weight average molecular
weight (M_w) less than about 20,000 based on the
combined weight of the first set of the at least one
or more polymeric compounds and the second set of the
at least one or more polymeric compounds.

44.   The process of Claim 43, wherein at least
80% by weight of the first and second sets of
polymeric compounds in the composition have a weight
average molecular weight (M_w) less than about 15,000
based on the combined weight of the first set of the
at least one or more polymeric compounds and

the second set of the at least one or more polymeric
compounds.

45.   The process of Claim 43, wherein at least
85% by weight of the first and second sets of
polymeric compounds in the composition have a weight
average molecular weight (M_w) less than about 10,000
based on the combined weight of the first set of the
at least one or more polymeric compounds and the
second set of the at least one or more polymeric
compounds.

46.   The process of Claim 40, wherein the
composition (a) and the solvent (c) have a solubility
with the at least one subcritical compressed fluid of
at least about 10% by weight of the subcritical
compressed fluid in the liquid mixture formed.

47.   The process of Claim 46, wherein the
solubility is at least about 15% by weight of the
subcritical compressed fluid in the liquid mixture
formed.

48.   The process of Claim 46, wherein the
solubility is in the range of from about 20 to about
70% by weight of the subcritical compressed fluid in
the liquid mixture formed.

49.   The process of Claim 40, wherein the
viscosity of the mixture of (a), (b) and (c) is less
than about 150 cps.

50.   The process of Claim 49, wherein the
viscosity of the mixture of (a), (b) and (c) is less

than about 100 cps.

51.   The process of Claim 49, wherein the
viscosity of the mixture of (a), (b) and (c) is in
the range of from about 1 to about 75 cps.

52.   The process of Claim 40, wherein the amount
of active solvent is present in an amount such that
the viscosity of (a) and (c) is greater than about
150 cps but less than about 4,000 cps.

53.   The process of Claim 52, wherein the
viscosity of the mixture of (a) and (c) is less than
about 2,000.

54.   The process of Claim 40, wherein the at
least one subcritical compressed fluid comprises
carbon dioxide.

55.   The process of Claim 40, wherein the at
least one subcritical compressed fluid comprises
nitrous oxide.

56.   The process of Claim 40, wherein the at
least one subcritical compressed fluid comprises a
mixture of carbon dioxide and nitrous oxide.

57.   The process of Claim 40, wherein the liquid
mixture is formed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is greater than about 0.1.

58.   The process of Claim 57, wherein the liquid
mixture is formed at temperatures such that the

subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is greater than about 0.25.

59.   The process of Claim 40, wherein the liquid
mixture is formed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.8 when the
pressure is greater than the critical pressure of the
subcritical compressed fluid.

60.   The process of Claim 59, wherein the liquid
mixture is formed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.6 when the
pressure is greater than the critical pressure of the
subcritical compressed fluid.

61.   The process of Claim 40, wherein the liquid
mixture is formed at temperatures which are less than
about 20 degrees C above the critical temperature of
the subcritical compressed fluid when the pressure is
less than the critical pressure of the subcritical
compressed fluid.

62.   The process of Claim 61, wherein the liquid
mixture is formed at temperatures which are less than
about 10 degrees C above the critical temperature of
the subcritical compressed fluid when the pressure is
less than the critical pressure of the subcritical
compressed fluid.

63.   The process of Claim 40, wherein the liquid
mixture is formed at substantially ambient
temperature.

64.   The process of Claim 40, wherein the liquid
mixture is formed at a pressure less than about 95%
of the absolute critical pressure of the subcritical
compressed fluid when the temperature is above the
critical temperature of the subcritical compressed
fluid.

65.   The process of Claim 64, wherein the liquid
mixture is formed at a pressure in the range of from
about 50 to about 90% of the absolute critical
pressure of the subcritical compressed fluid when the
temperature is above the critical temperature of the
subcritical compressed fluid.

66.   The process of Claim 40, wherein the liquid
mixture is formed at a pressure less than about 600
psi above the critical pressure of the subcritical
compressed fluid when the temperature is less than
the critical temperature of the subcritical
compressed fluid.

67.   The process of Claim 40, wherein the liquid
mixture is formed at a pressure in the range of from
about 500 to about 1020 psi when the subcritical
compressed fluid is carbon dioxide.

68.   The process of Claim 67, wherein the liquid
mixture is formed at a pressure in the range of from
about 700 to about 970 psi when the subcritical
compressed fluid is carbon dioxide.

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69.   The process of Claim 40, wherein said one or more polymeric compounds are selected from the group consisting of acrylics, polyesters, melamines, alkyds, epoxies urethanes, urea formaldehydes, vinyls, silicone polymers and mixtures thereof.

70.   The process of Claim 40, wherein the at least one active solvent is selected from the group consisting of aliphatic or aromatic hydrocarbons, ketones, esters, ethers, alcohols and mixtures thereof.

71.   The process of Claim 70, wherein the active solvent is a glycol ether.

72.   The process of Claim 70, wherein the liquid mixture includes an additive selected from the group consisting of pigments, drying agents, anti-skinning agents, and combinations thereof.

73.   The process of Claim 40, wherein at least one of the one or more polymeric compounds is a silicon containing polymer.

74.   The process of Claim 40, wherein the at least one of the one or more polymeric compounds is a fluorine containing polymer.

75.   A process for the liquid spray application of coatings to a substrate, which comprises:

　　　a)   forming a liquid mixture in a closed system, said liquid mixture comprising:

　　　　i)   a first set of at least one or more liquid polymeric compounds wherein the

number-average molecular weight (M_n) of the
one or more liquid polymeric compounds is
less than about 5,000; and

      ii) at least one subcritical
compressed fluid in at least an amount which
when added to (i) is sufficient to render
the viscosity of said mixture to a point
suitable for being transportable, wherein
the subcritical compressed fluid is a gas at
standard conditions of $0^\circ C$ and one
atmosphere (STP); and

     b) spraying said liquid mixture onto a
substrate to form a liquid coating thereon having
substantially the composition of the said coating
formulation.

76.   The process of Claim 75, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
3,500.

77.   The process of Claim 76, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
2,500.

78.   The process of Claim 75, wherein a second
set of one or more polymeric compounds are contained
in the liquid mixture wherein at least 75% by weight
of the first and second sets of polymeric compounds
in the liquid mixture have a weight average molecular
weight (M_w) less than about 20,000 based on the
combined weight of the first set of the at least one

or more liquid polymeric compounds and the second set
of the at least one or more polymeric compounds.

79.   The process of Claim 78, wherein at least
80% by weight of the first and second sets of
polymeric compounds in the liquid mixture have a
weight average molecular weight (M_W) less than about
15,000 based on the combined weight of the first set
of the at least one or more liquid polymeric
compounds and the second set of the at least one or
more polymeric compounds.

80.   The process of Claim 78, wherein at least
85% by weight of the first and second sets of
polymeric compounds in the liquid mixture have a
weight average molecular weight (M_W) less than about
10,000 based on the combined weight of the first set
of the at least one or more liquid polymeric
compounds and the second set of the at least one or
more polymeric compounds.

81.   The process of Claim 75, wherein the
solubility is at least about 10% by weight of the
subcritical compressed fluid in the liquid mixture
formed.

82.   The process of Claim 81, wherein the
solubility is at least about 15% by weight of the
subcritical compressed fluid in the liquid mixture
formed.

83.   The process of Claim 81, wherein the
solubility is in the range of from about 20 to about

70% by weight of the subcritical compressed fluid in the liquid mixture formed.

84.   The process of Claim 75, wherein the viscosity of the mixture of (i) and (ii) is less than about 150 cps.

85.   The process of Claim 75, wherein the viscosity of the mixture of (i) and (ii) is less than about 100 cps.

86.   The process of Claim 85, wherein the viscosity of the mixture of (i) and (ii) ranges from about 1 to about 75 cps.

87.   The process of Claim 75 further comprising adding to said liquid mixture at least one active solvent (iii) in which said at least one or more polymeric compounds (i) are at least partially soluble and which is at least partially miscible with the subcritical compressed fluid (ii), said solvent being present in an amount such that the viscosity of (i) and (iii) is greater than about 150 cps but less than about 4,000 cps.

88.   The process of Claim 87, wherein the viscosity of the mixture of (i) and (iii) is less than about 2,000 cps.

89.   The process of Claim 87, wherein the viscosity of the mixture of (i), (ii) and (iii) is less than about 150 cps.

90.   The process of Claim 89, wherein the viscosity of the mixture of (i), (ii) and (iii) is

less than about 100 cps.

91.   The process of Claim 90, wherein the
viscosity of the mixture of (i), (ii) and (iii) is
from about 1 to about 75 cps.

92.   The process of Claims 75 or 87, wherein the
at least one subcritical compressed fluid comprises
carbon dioxide.

93.   The process of Claims 75 or 87, wherein the
at least one subcritical compressed fluid comprises
nitrous oxide.

94.   The process of Claims 75 or 87, wherein the
at least one subcritical compressed fluid comprises a
mixture of carbon dioxide and nitrous oxide.

95.   The process of Claim 75, wherein the liquid
mixture is sprayed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is greater than about 0.1.

96.   The process of Claim 95, wherein the liquid
mixture is sprayed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is greater than about 0.25.

97.   The process of Claim 75, wherein the liquid
mixture is sprayed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.8 when the

pressure is greater than the critical pressure of the subcritical compressed fluid.

98.   The process of Claim 97, wherein the liquid mixture is sprayed at temperatures such that the subcritical compressed fluid has a ratio of gas density to liquid density at equilibrium at such temperatures which is less than about 0.6 when the pressure is greater than the critical pressure of the subcritical compressed fluid.

99.   The process of Claim 75, wherein the liquid mixture is sprayed at temperatures which are less than about 20 degrees C above the critical temperature of the subcritical compressed fluid when the pressure is less than the critical pressure of the subcritical compressed fluid.

100.   The process of Claim 99, wherein the liquid mixture is sprayed at temperatures which are less than about 10 degrees C above the critical temperature of the subcritical compressed fluid when the pressure is less than the critical pressure of the subcritical compressed fluid.

101.   The process of Claim 75, wherein the liquid mixture is sprayed at substantially ambient temperature.

102.   The process of Claim 75, wherein the liquid mixture is sprayed at a pressure less than about 95% of the absolute critical pressure of the subcritical compressed fluid when the temperature is above the critical temperature of the subcritical compressed fluid.

103.   The process of Claim 102, wherein the liquid
mixture is sprayed at a pressure in the range of from
about 50 to about 90% of the absolute critical
pressure of the subcritical compressed fluid when the
temperature is above the critical temperature of the
subcritical compressed fluid.

104.   The process of Claim 75, wherein the liquid
mixture is sprayed at a pressure less than about 600
psi above the critical pressure of the subcritical
compressed fluid when the temperature is less than
the critical temperature of the subcritical
compressed fluid.

105.   The process of Claim 75, wherein the liquid
mixture is sprayed at a pressure in the range of from
about 500 to about 1020 psi when the subcritical
compressed fluid is carbon dioxide.

106.   The process of Claim 105, wherein the liquid
mixture is formed at a pressure in the range of from
about 700 to about 970 psi when the subcritical
compressed fluid is carbon dioxide.

107.   The process of Claim 75, wherein said one or
more polymeric compounds are selected from the group
consisting of acrylics, polyesters, melamines,
alkyds, epoxies urethanes, urea formaldehydes,
vinyls, silicone polymers and mixtures thereof.

108.   The process of Claim 87, wherein the at
least one active solvent is selected from the group
consisting of aliphatic or aromatic hydrocarbons,

ketones, esters, ethers, alcohols and mixtures
thereof.

109.   The process of Claim 108, wherein the active
solvent is a glycol ether.

110.   The process of Claim 75, wherein the liquid
mixture includes an additive selected from the group
consisting of pigments, drying agents, anti-skinning
agents, and combinations thereof.

111.   The process of Claim 75, wherein at least
one of the one or more polymeric compounds is a
silicon containing polymer.

112.   The process of Claim 75, wherein the at
least one of the one or more polymeric compounds is a
fluorine containing polymer.

113.   The process of Claim 75, wherein the liquid
mixture is sprayed as a feathered spray.

114.   The process of Claim 75, wherein the liquid
mixture is sprayed with decompressive atomization.

115.   The process of Claim 75, wherein at liquid
mixture is sprayed electrostatically.

116.   The process of Claim 75, wherein after being
sprayed, the subcritical compressed fluid has a
solubility with the sprayed liquid polymeric
compounds of less than about 0.8% by weight of the
fluid, in the non-subcritical compressed state.

117.   The process of Claim 116, wherein the
solubility with the sprayed liquid polymeric
compounds is less than about 0.6% by weight of the
fluid, in the non-compressed state.

118.   A process for the liquid spray application
of coatings to a substrate, which comprises:
        a)   forming a liquid mixture in a closed
system, said liquid mixture comprising:
            i)   a first set of at least one or
        more polymeric compounds capable of forming
        a coating on a substrate wherein the number
        average molecular weight (M_n) of the one or
        more polymeric compounds is less than about
        5,000; and
            ii)   at least one subcritical
        compressed fluid in at least an amount which
        when added to (i) and (iii) is sufficient to
        render the viscosity of said mixture to a
        point suitable for spray application,
        wherein the subcritical compressed fluid is
        a gas at standard conditions of $0^{o}C$ and one
        atmosphere (STP); and
            iii) at least one active solvent in
        which said one or more polymeric compounds
        are at least partially soluble and which is
        at least partially miscible with the
        subcritical compressed fluid (ii), said
        solvent being present in an amount such that
        the viscosity of (i) and (iii) is greater
        than than desirable for liquid spray
        applications; and
        b)   spraying said liquid mixture onto a
substrate to form a liquid coating thereon.

119.   The process of Claim 118, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
3,500.

120.   The process of Claim 119, wherein the one or
more polymeric compounds of the first set have a
number average molecular weight (M_n) less than about
2,500.

121.   The process of Claim 118, wherein a second
set of one or more polymeric compounds are contained
in the mixture wherein at least 75% by weight of the
first and second sets of polymeric compounds in the
liquid mixture have a weight average molecular weight
(M_w) less than about 20,000 based on the combined
weight of the first set of the at least one or more
polymeric compounds and the second set of the at
least one or more polymeric compounds.

122.   The process of Claim 121, wherein at least
80% by weight of the first and second sets of
polymeric compounds in the liquid mixture have a
weight average molecular weight (M_w) less than about
15,000 based on the combined weight of the first set
of the at least one or more polymeric compounds and
the second set of the at least one or more polymeric
compounds.

123.   The process of Claim 121, wherein at least
85% by weight of the first and second sets of
polymeric compounds in the liquid mixture have a
weight average molecular weight (M_w) less than

about 10,000 based on the combined weight of the first set of the at least one or more polymeric compounds and the second set of the at least one or more polymeric compounds.

124.   The process of Claim 118, wherein the liquid polymeric compounds (i) and active solvent (iii) have a solubility with the at least one subcritical compressed fluid of at least about 10% by weight of the subcritical compressed fluid in the liquid mixture formed.

125.   The process of Claim 118, wherein the viscosity of the mixture of (i), (ii) and (iii) is less than about 150 cps.

126.   The process of Claim 118, wherein the at least one subcritical compressed fluid comprises carbon dioxide.

127.   The process of Claim 118, wherein the liquid mixture is sprayed at temperatures such that the subcritical compressed fluid has a ratio of gas density to liquid density at equilibrium at such temperatures which is greater than about 0.1.

128.   The process of Claim 127, wherein the liquid mixture is sprayed at temperatures such that the subcritical compressed fluid has a ratio of gas density to liquid density at equilibrium at such temperatures which is greater than about 0.25.

129.   The process of Claim 118, wherein the liquid mixture is sprayed at temperatures such that the

subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.8 when the
pressure is greater than the critical pressure of the
subcritical compressed fluid.

130.   The process of Claim 129, wherein the liquid
mixture is sprayed at temperatures such that the
subcritical compressed fluid has a ratio of gas
density to liquid density at equilibrium at such
temperatures which is less than about 0.6 when the
pressure is greater than the critical pressure of the
subcritical compressed fluid.

131.   The process of Claim 118, wherein the liquid
mixture is sprayed at temperatures which are less
than about 20 degrees C above the critical
temperature of the subcritical compressed fluid when
the pressure is less than the critical pressure of
the subcritical compressed fluid.

132.   The process of Claim 131, wherein the liquid
mixture is sprayed at temperatures which are less
than about 10 degrees C above the critical
temperature of the subcritical compressed fluid when
the pressure is less than the critical pressure of
the subcritical compressed fluid.

133.   The process of Claim 118, wherein the liquid
mixture is sprayed at substantially ambient
temperature.

134.   The process of Claim 118, wherein the liquid
mixture is sprayed at a pressure less than about 95%

of the absolute critical pressure of the subcritical compressed fluid when the temperature is above the critical temperature of the subcritical compressed fluid.

135.   The process of Claim 134, wherein the liquid mixture is sprayed at a pressure in the range of from about 50 to about 90% of the absolute critical pressure of the subcritical compressed fluid when the temperature is above the critical temperature of the subcritical compressed fluid.

136.   The process of Claim 118, wherein the liquid mixture is sprayed at a pressure less than about 600 psi above the critical pressure of the subcritical compressed fluid when the temperature is less than the critical temperature of the subcritical compressed fluid.

137.   The process of Claim 118, wherein the liquid mixture is sprayed at a pressure in the range of from about 500 to about 1020 psi when the subcritical compressed fluid is carbon dioxide.

138.   The process of Claim 137, wherein the liquid mixture is formed at a pressure in the range of from about 700 to about 970 psi when the subcritical compressed fluid is carbon dioxide.

139.   The process of Claim 118, wherein at least one of the one or more polymeric compounds is a silicon containing polymer.

140.   The process of Claim 118, wherein the at least one of the one or more polymeric compounds is a fluorine containing polymer.

141.   The process of Claim 118, wherein the liquid mixture is sprayed as a feathered spray.

142.   The process of Claim 118, wherein the liquid mixture is sprayed with decompressive atomization.

143.   The process of Claim 118, wherein at liquid mixture is sprayed electrostatically.

144.   The process of Claim 118, wherein after being sprayed, the subcritical compressed fluid has a solubility with the sprayed liquid mixture of less than about 0.8% by weight of the fluid, in the non-compressed state.

145.   The process of Claim 118, wherein the viscosity of (i) and (iii) is less than about 6000 cps.

Fig. 1
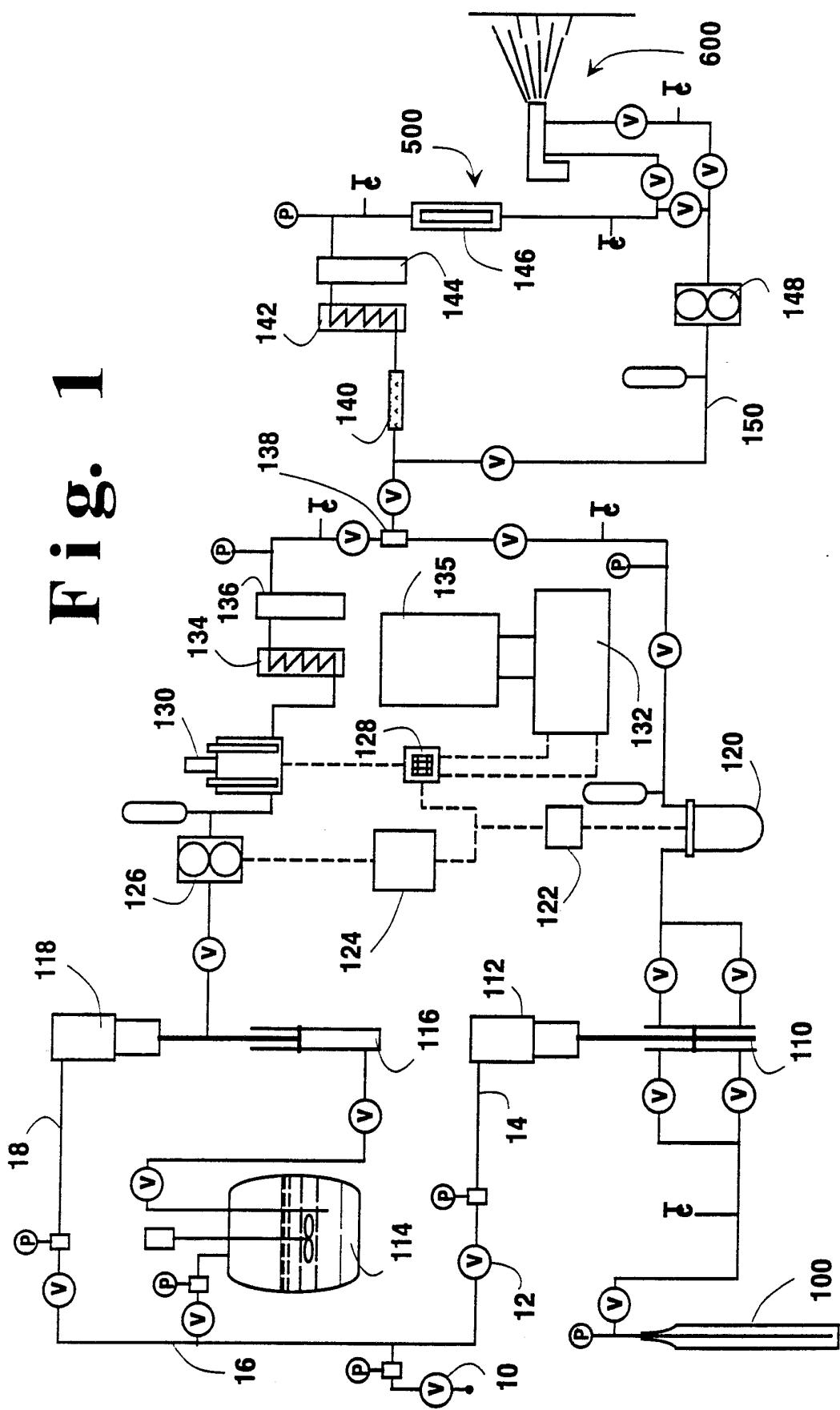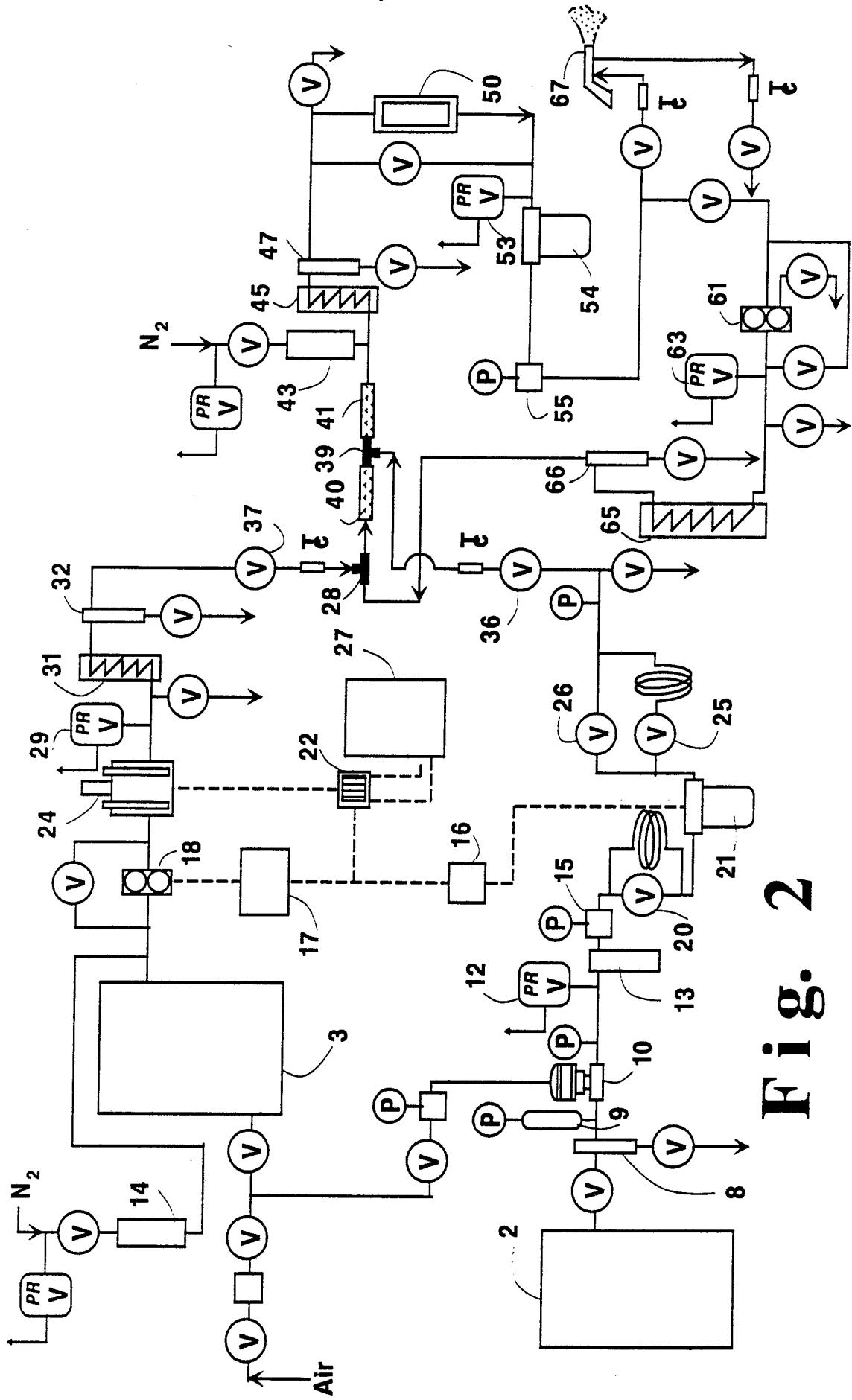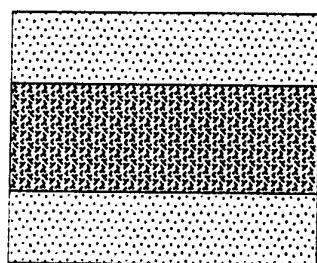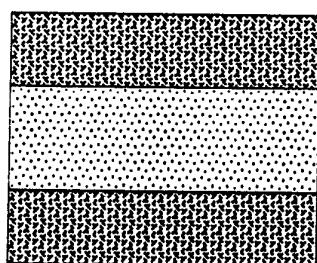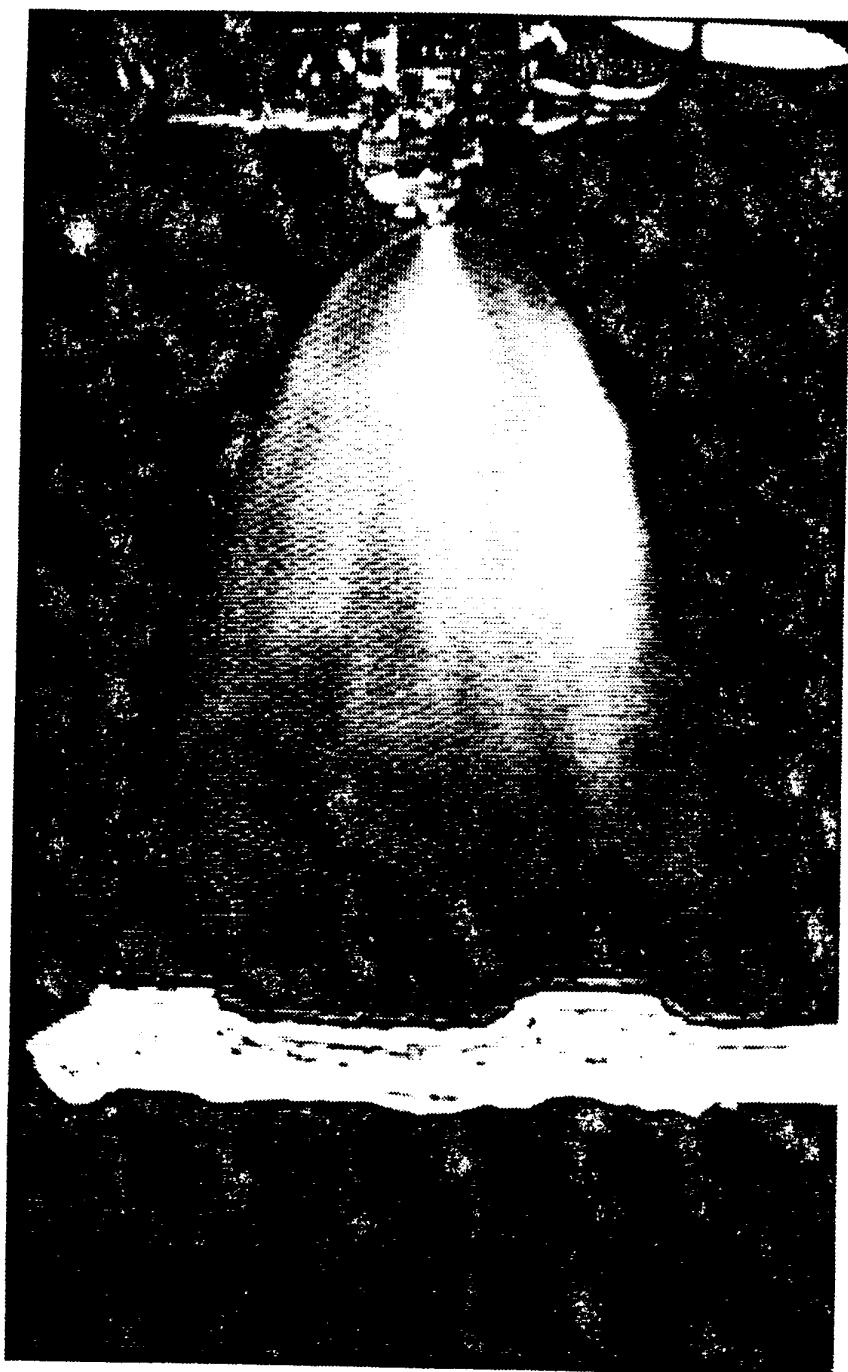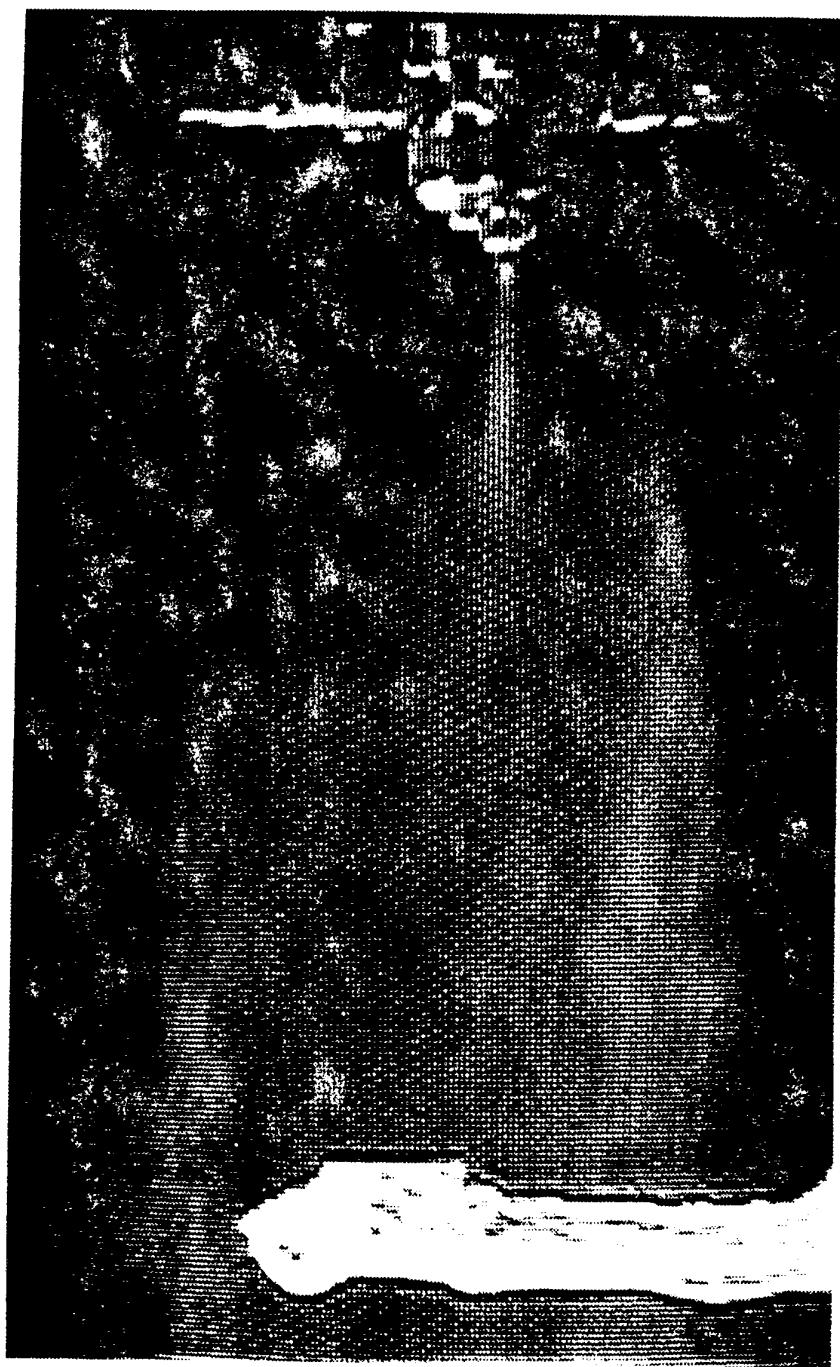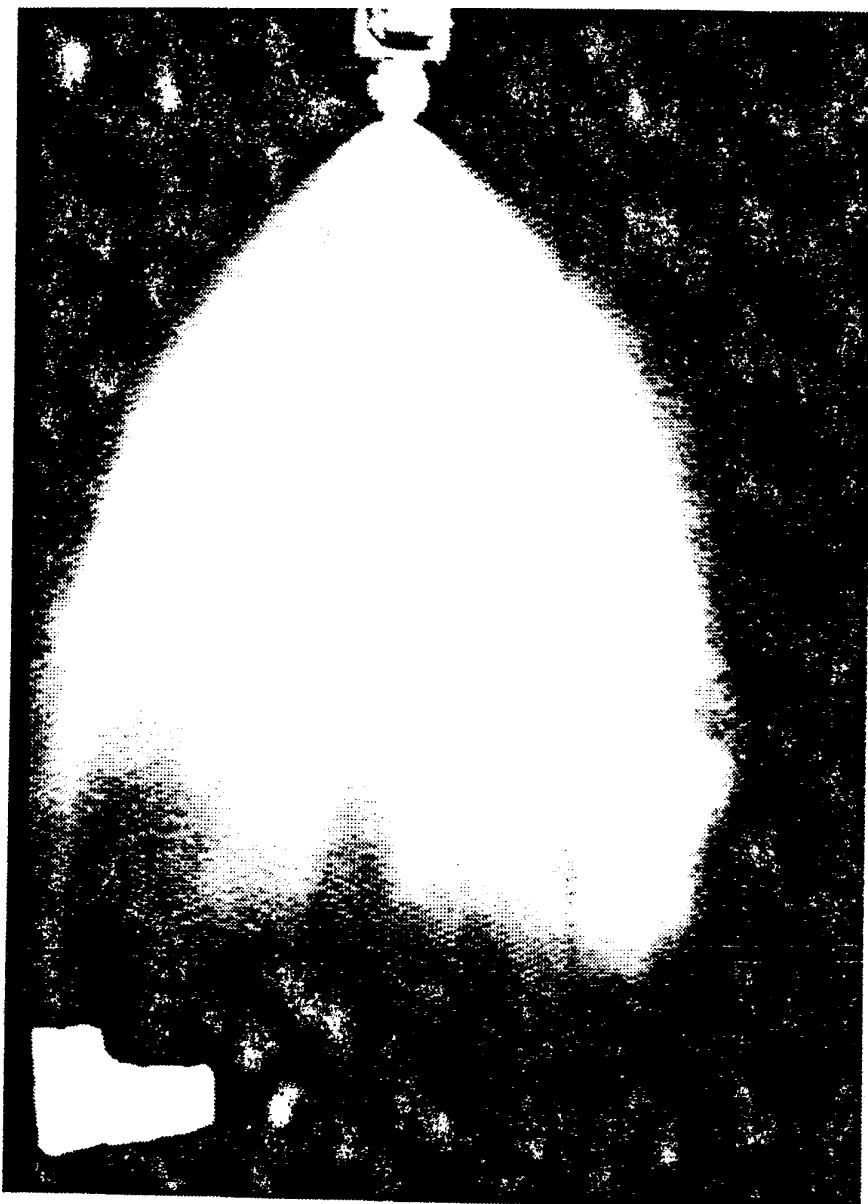
Fig. 2

Fig. 3

Fig. 4

F I G. 5a

F I G. 5b

F I G. 5c

# F I G. 5d

F I G. 5e

F I G. 5f
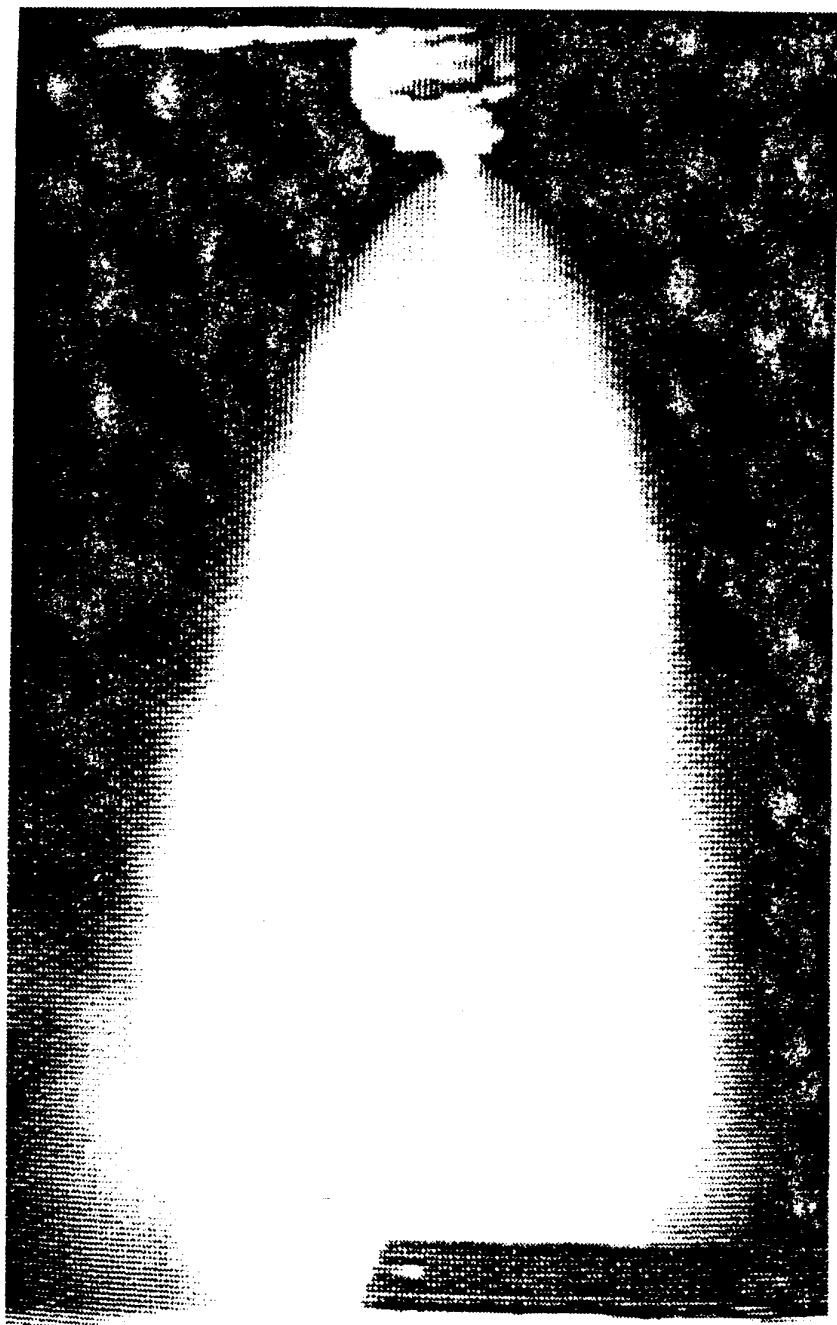
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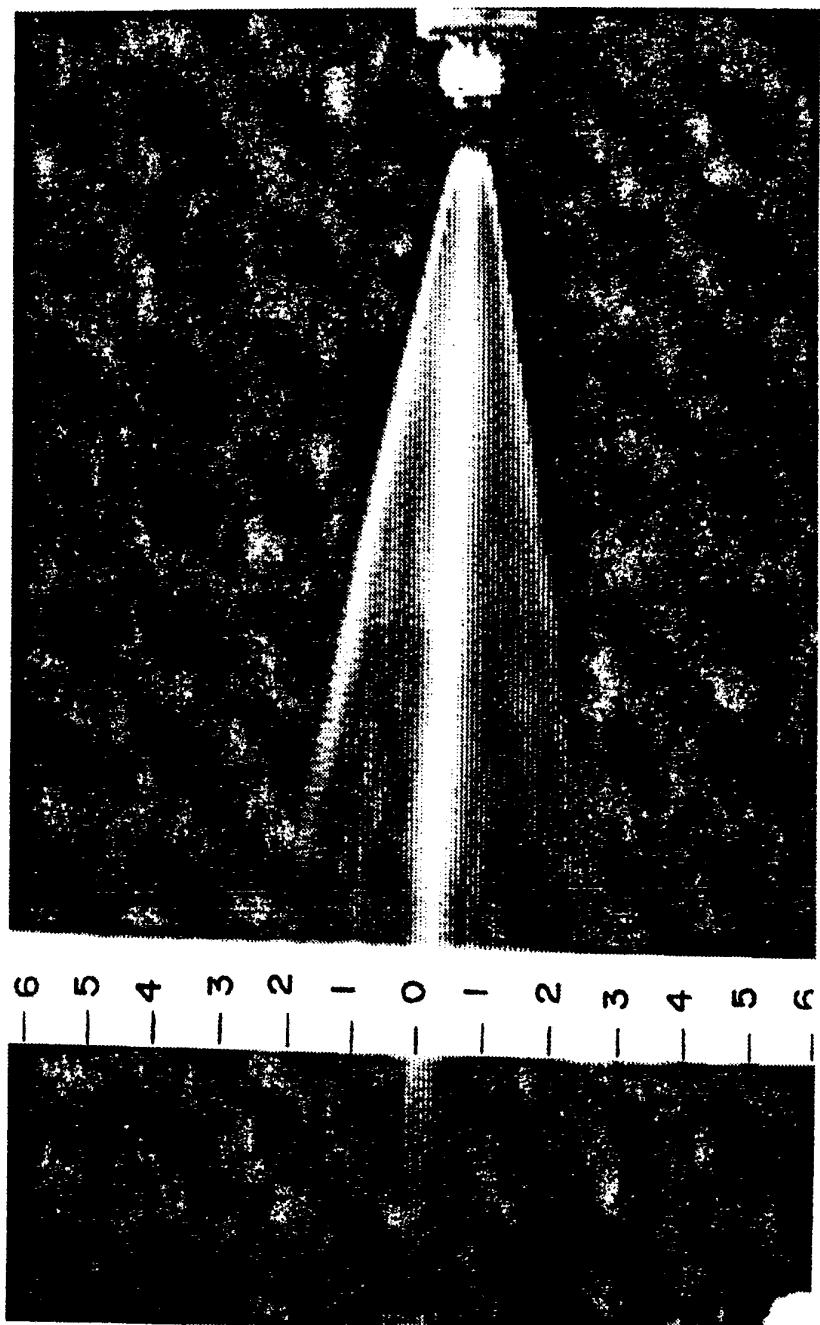
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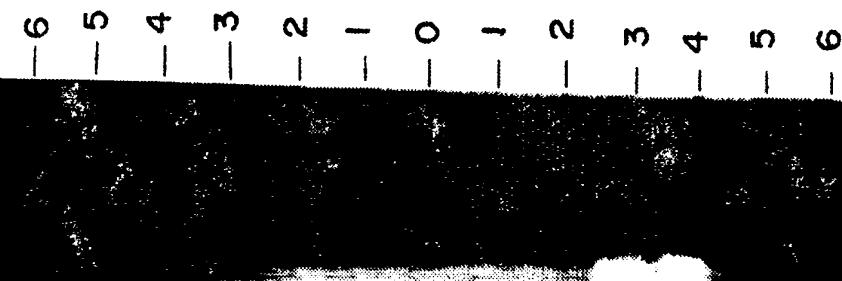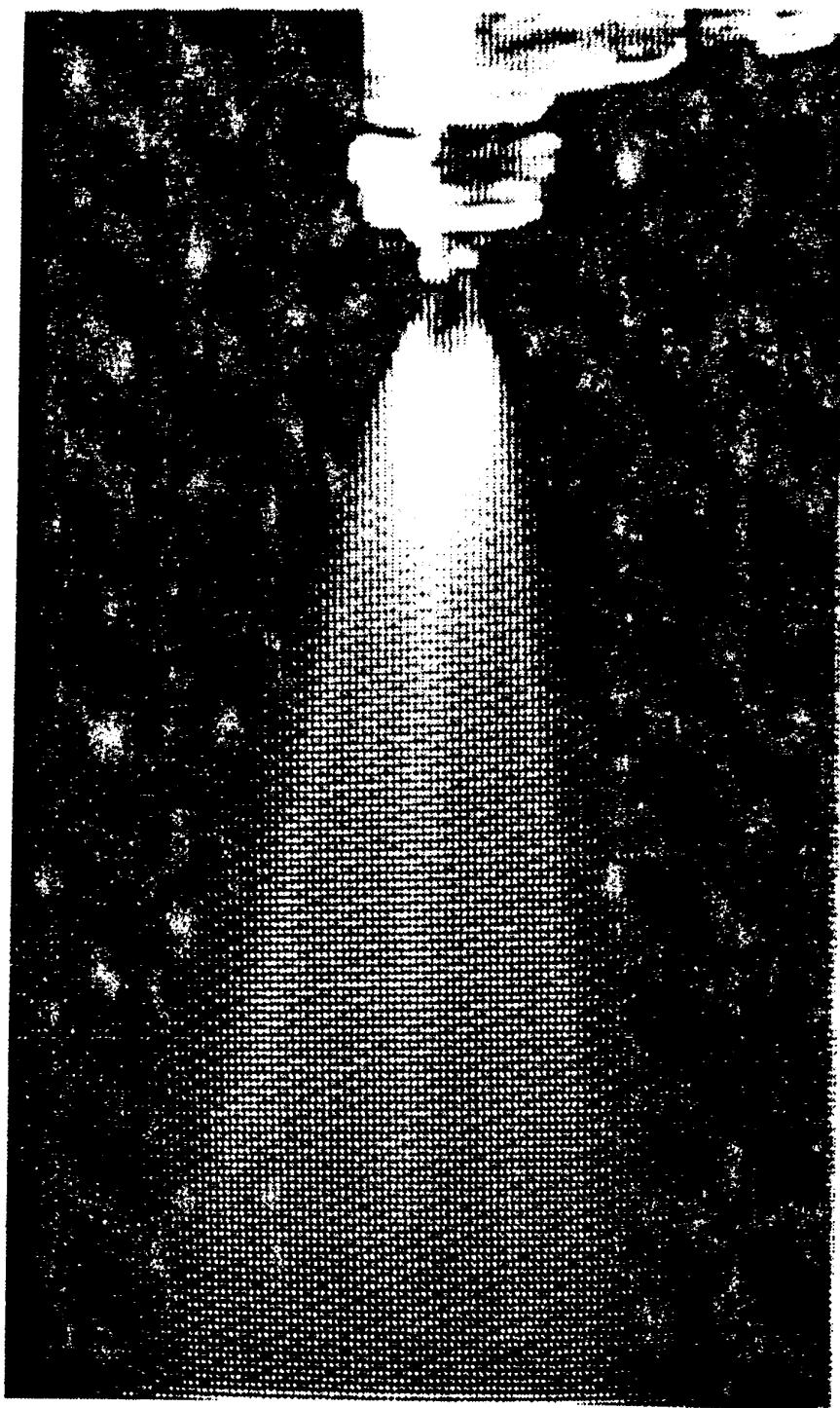
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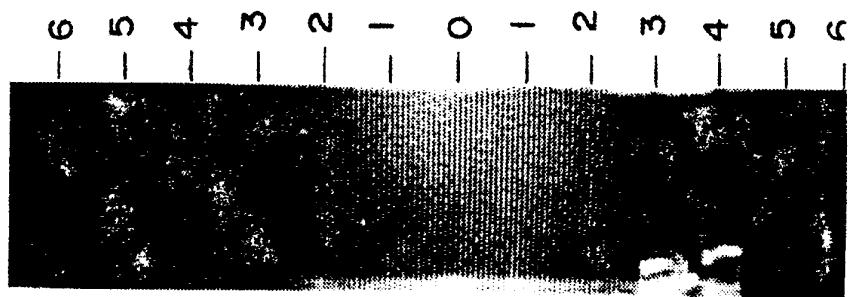
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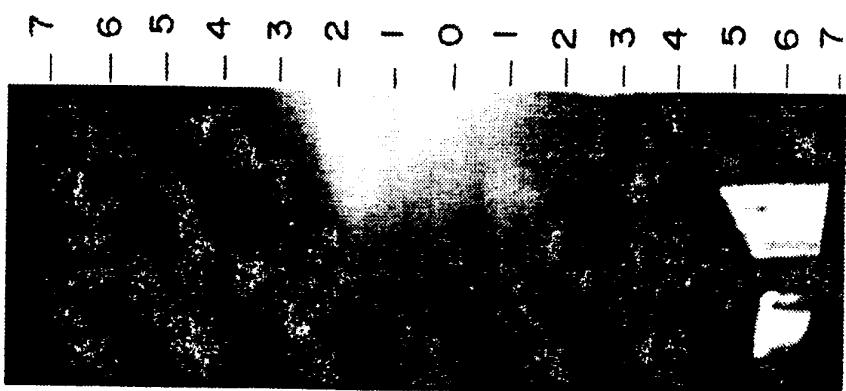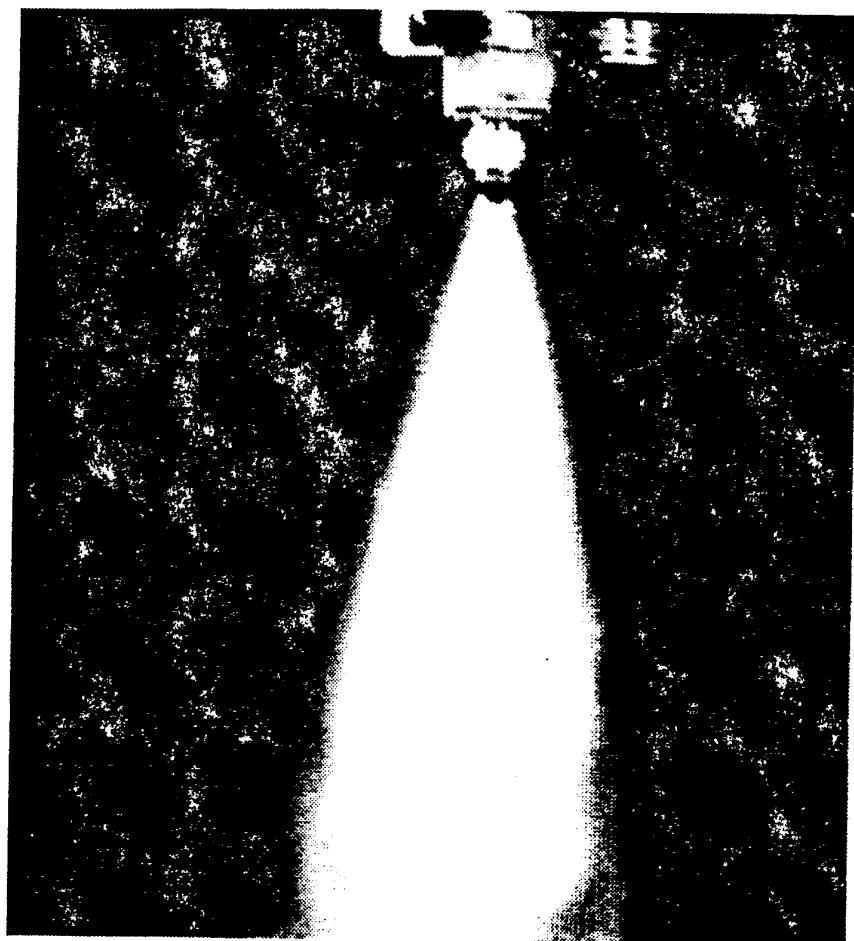
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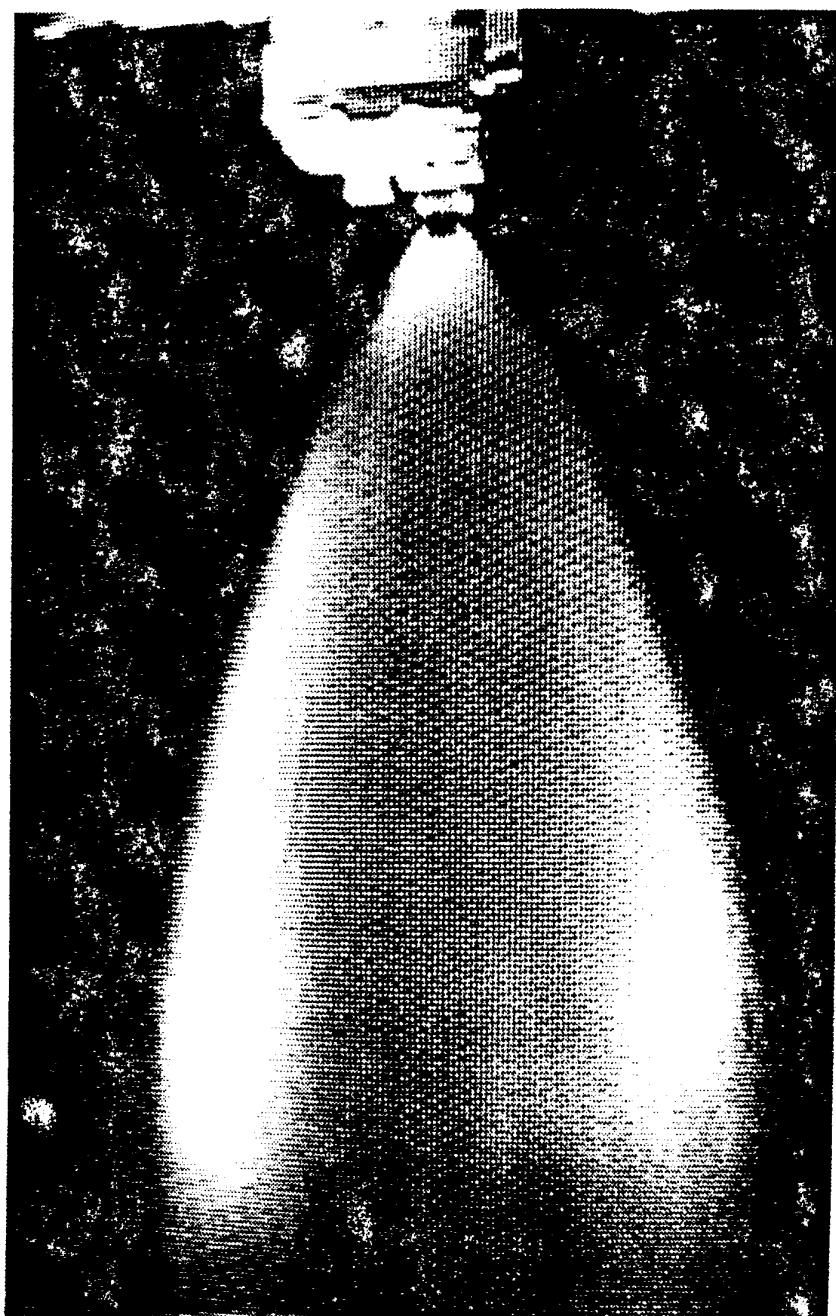
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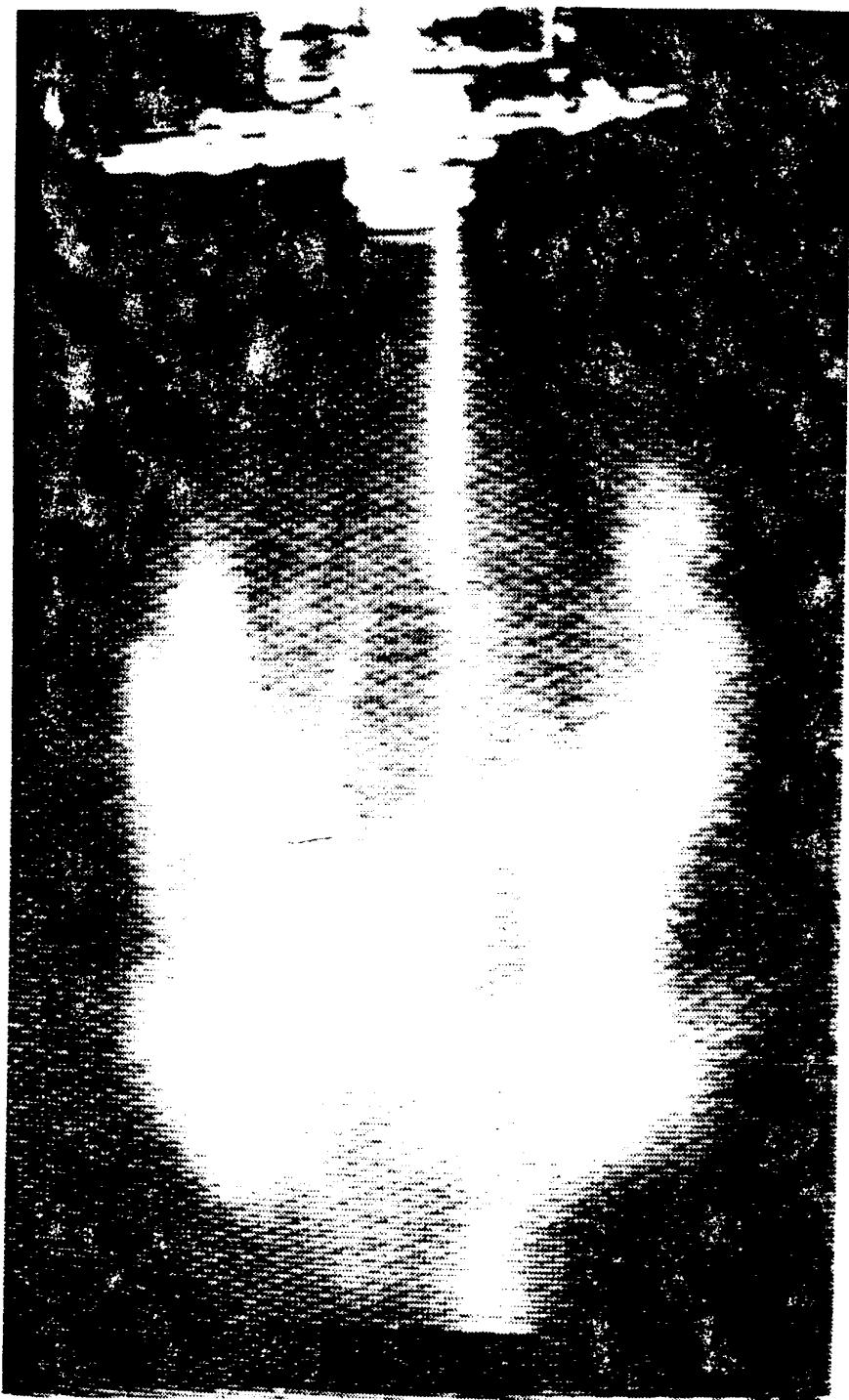
F I G. 7a

F I G. 7b

## TEMPERATURE PROFILE OF SPRAY AS A FUNCTION OF DISTANCE FROM SPRAY TIP
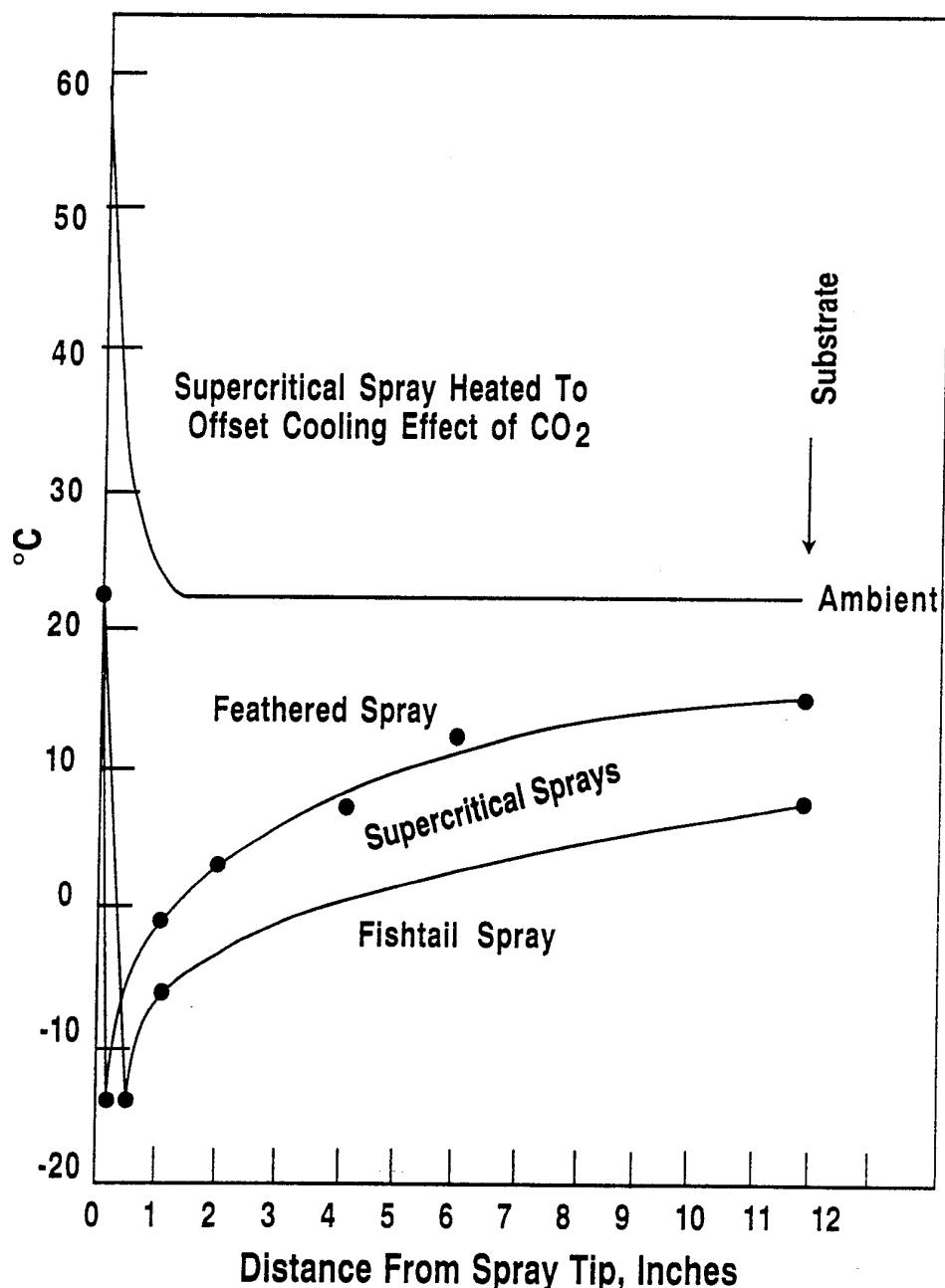
Fig. 8

CARBON DIOXIDE SOLUBILITY AS A FUNCTION
OF PRESSURE AT CONSTANT TEMPERATURE
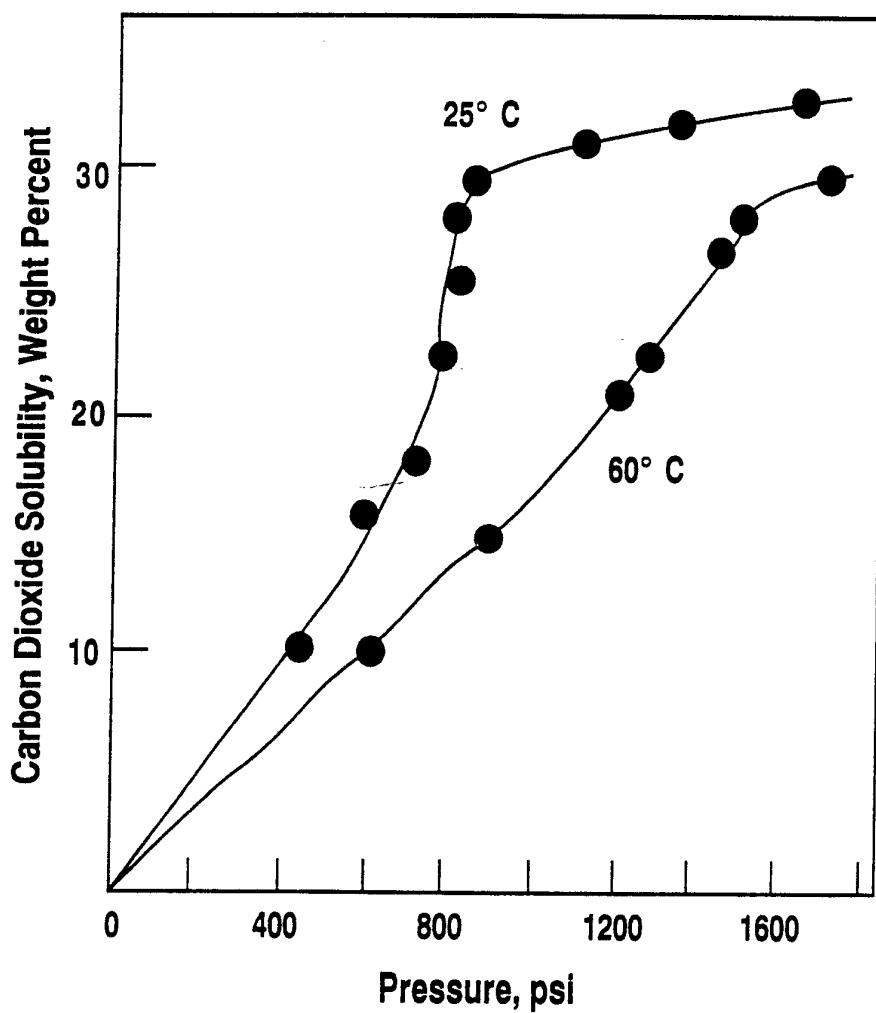
Fig. 9

VISCOSITY REDUCTION BY DISSOLVED
CARBON DIOXIDE
AT TEMPERATURE OF 25° C

Weight-Percent Concentration of Dissolved Carbon Dioxide

F i g. 10