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SOLVENT BROKE

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The title "Solvent Broke" was selected to call to the attention of TAPPI members the idea that broke need not be cellulosic.

Activated carbon adsorption has been used for 40 years in the U.S.A. to recover a wide variety of solvents from solvent laden air streams. We will discuss in particular solvent recovery applications presently on stream, or feasible in the paper industry. Equipment and process will be described. Criteria for evaluating Solvent Recovery to specific applications will be provided.

The topic "Solvent Broke" is intended to direct the attention of the paper producing and paper converting industry to the re-use of solvents which they may presently be using on a once through basis and then exhausting to atmosphere. Just as cellulosic waste (broke) is recycled so can most solvents be recycled by reclaiming them with an activated carbon solvent recovery system which permits repeated re-use of the solvent (broke) which would otherwise be wasted to atmosphere.

STATE OF THE ART

The process of recovering solvents from air streams on activated carbon is not new. There are systems which have been in continuous operation for 40 years. Perhaps one of the earliest applications of activated carbon which became known to the general public was its use as the adsorbent material in gas masks during World War I. Our own library has many references to activated carbon predating the year 1910. It has been a topic in chemical engineering courses since the curriculum was initiated.

WHAT IS SOLVENT RECOVERY?

Simply stated, solvent recovery is a process in which solvent laden air is passed through a bed of activated carbon. The solvent(s) are adsorbed on the carbon and clean air is exhausted from the system. When the carbon has reached its capacity for holding solvent(s) it is desorbed with low pressure steam and the solvents recovered through the system can be re-used.

Solvent Recovery Equipment

Solvent recovery systems used in industrial applications, frequently have the following components:

Solvent Laden Air Filter - Where there is particulate in the solvent laden air stream, filters are used to remove it.

Solvent Laden Air Scrubber - This is used to remove resins or foreign material which can not be effectively removed in a filter.

Solvent Laden Air Cooler - When the temperature of the solvent laden air stream is excessive, a cooler is used to reduce its temperature to about 95°F before entering the activated carbon bed.

Solvent Laden Air Heater - When necessary this is used to heat a cold air stream or, to re-heat a solvent laden air stream which has been sub-cooled. Sub-cooling and re-heating is done to control humidity when the incoming solvent laden air stream has too high a moisture content.

Humidifier - This is installed when the incoming solvent laden air stream has too low a relative humidity.

Blower and Drive - A spark resistant blower frequently driven by a TEFC electric motor is used to force the solvent laden air through a carbon bed. Pressure drops through the carbon bed vary according to design, but are frequently in the range of 15" to 21" w.c.

Valves and Operators - Pneumatically operated valves are commonly used on the solvent laden air inlet stream, the air outlet, the steam inlet and the vapor outlet.

Adsorbers - Most systems use two or more adsorber vessels containing activated carbon.

Carbon - a charge of activated carbon for each adsorber. Two grams of activated carbon has the surface equivalent to 1 acre of ground.

Condenser - The condenser, frequently water cooled type, is used to cool and liquify the steam and solvent vapors exhausted from the adsorber vessel during the desorbing/steaming cycle.

Decanter - This is used to continuously separate the condensed solvent from the steam condensate when the solvents are not miscible with water.

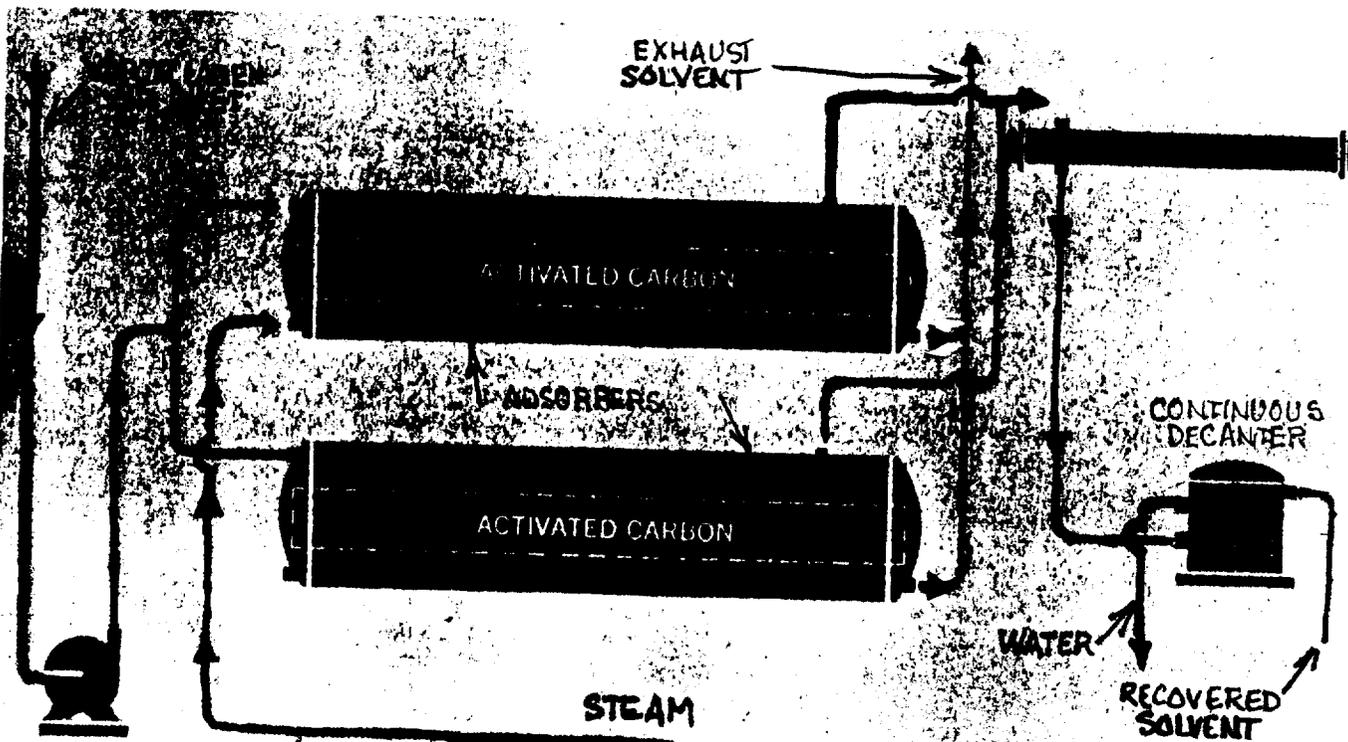
Receiving Tank - This is used to store recovered solvent(s) that are miscible with water.

Distillation Column - This may be used to separate water miscible solvents from water or to separate mixed solvents.

Instruments and Controls - The following items may be provided, however, this is not intended to represent a single installation or a complete listing:

Flame Arrestor - in the vent line from the condenser and decanter back to the blower inlet.

- Condensate Traps
- Condensate Pump(s)
- Solenoids
- Timer
- Analyzer
- Temperature Indicators and switches
- Pressure Indicators and switches
- Recorders - as required
- Audible alarm - Visual alarm
- Hand control valves
- Pressure reducing valves for steam
- Indicator lights and switches
- Control console.



FUNDAMENTAL FLOW DIAGRAM OF VULCAN-CINCINNATI'S
ACTIVATED CARBON SOLVENT RECOVERY SYSTEM

PROCESS DESCRIPTION

The flow diagram shown here is a typical two adsorber solvent recovery system. In this scheme, one adsorber is adsorbing solvent from the solvent laden air stream while the other is being desorbed/steamed and resting awaiting its turn for the adsorption phase. When the carbon in the vessel adsorbing has reached its capacity for solvent, the solvent laden air stream is automatically directed to the other vessel. This cycle can be controlled by an analyzer or a timer. When the appropriate valve position changes have been made the vessel which has just completed its adsorption phase, is steamed counter current to the solvent laden air flow. During the heat-up process, about half of the steam condenses and exits the adsorber vessel through a steam trap. After heat up the steam and solvent vapors are directed to a condenser which cools and liquifies the vapors. It is then directed to the decanter where those solvents which are not water miscible are continuously separated from the steam condensate. The solvents may flow back to solvent storage and the water condensate may be used as boiler feed water, cooling tower make-up, or be sewerred. Where the solvents are water miscible the condensate from the condenser flows to a receiving tank where it is held for further processing, perhaps distillation.

What Solvents Can be Recovered

Generally speaking all organic vapors can be recovered from an air stream. Carbon is not selective, therefore, all solvents present in an air stream will be adsorbed on the carbon. It is important to note that the carbon does have varying capacities for different solvents.

Acetone is one of the solvents very often recovered. It is safe to say that the rayon industry would not have been possible without the economies realized from the recovery of acetone. This industry is a large and enthusiastic user of activated carbon solvent recovery systems.

Following is a partial list of solvents which are satisfactorily being recovered today.

Toluene
Ethyl Acetate
MEK
Acetone
Xylene
Acetate
Heptane

Naphtha
Naphthol Spirits
MIBK
THF
Freon
Benzene
Methylene Chloride
Ketones
VMP
Cellusolve
Isopropyl Alcohol

There are a number of solvent recovery plants owned and operated by those in the paper producing and paper converting industries. Solvents are recovered from coating, saturating and printing operations. Some of the solvents being recovered, and re-used by the paper industry are:

MEK
MIBK
Toluene
Ethyl Acetate
Ethyl alcohol
Xylene
Heptane

Problem Areas

While all solvents will be adsorbed by activated carbon, there are those for which the carbon has only a small capacity. One of these problems recently faced was the adsorption of methyl bromide. A solvent recovery system using activated carbon has been designed to recover this material. The design is complicated and the system is costly. High boilers, i.e., solvents with a relatively high boiling point, are readily adsorbed on carbon but are not so easily desorbed. Here again, the problems can be overcome but the equipment necessary to do the job becomes very complex and expensive. As the boiling point of a solvent approaches 400°F the problems of desorption increase greatly.

There are often foreign materials in a solvent laden air stream which can interfere with the adsorptive capacity of the carbon. Varnishes or resins which polymerize on the carbon bed must be removed before the solvent air stream enters the carbon bed. Another material occasionally encountered is DOP. This can not be permitted to enter the adsorption system for the life of the carbon will be decreased.

High humidity in the solvent laden air stream interferes with the proper operation of the system. There is a heat of adsorption which is different for each solvent. The

evaporation of the moisture from a carbon bed is used as a heat sink during the adsorption cycle. If a moisture saturated solvent laden air stream enters the carbon bed, not only will the moisture in the bed remain there, but this moisture will also occupy sites needed for the adsorption of the solvent.

Carbon Life

In most solvent recovery systems a life of 5 to 10 years is expected for the carbon. On Acetone recovery a life of 4 or 5 years is common. We know of one adsorption system which is still operating efficiently using carbon that is 18 years old. If the solvent laden air stream is reasonably free of contaminants, carbon life greater than 5 years can be anticipated. The normal aging process of carbon is oxidation. By operating a solvent recovery system continuously at high temperatures, say above 120°F the oxidation rate increases, thus accelerating the aging process which reduces the activity of the carbon. When this occurs the carbon must be replaced.

Lower Explosive Limits of Various Solvents

In selecting the air handling capacity of a recovery installation, consideration must be given to the lower explosive limit (LEL) concentration in air of the specific solvent or solvent mixture being handled. Sufficient air volume must be provided so that the concentration of solvent in the exhaust air from the vaporization process is maintained below the LEL in accordance with general safe practice, state and local ordinances, and insurance company requirements. The exact percentages of the LEL that can be considered acceptable will vary with vaporization processes. Normally, a design concentration of 25 to 40 per cent of the LEL is satisfactory.

The temperature of 70°C has been selected as representative of the evaporation temperatures most frequently used in manufacturing operations. Values shown as per cent by volume have been corrected to pounds of solvent per 1000 cubic feet of air-solvent mixture measured at 100°F and 1 atmosphere. (Recovery plant air flow is usually measured at this temperature.)

LEL OF MIXTURE IN POUNDS
PER 1000 CUBIC FEET AT 100°F
AND 1 ATMOSPHERE PRESSURE

$$= \frac{100}{\frac{\text{WT. \% A}}{\text{LEL A}} + \frac{\text{WT. \% B}}{\text{LEL B}} + \frac{\text{WT. \% C}}{\text{LEL C}} + \dots}$$

Solvent	LOWER EXPLOSIVE LIMIT IN AIR (APPROX. 1 ATMOS.)	
	Percent by Volume	Calc. lbs/1000 cu. ft. at 100°F
n-Pentane	1.30	2.30
n-Hexane	0.96	2.03
n-Heptane	0.96	2.36
n-Octane	0.88	2.46
Gasoline (Naphtha "R," 136-268°F)	0.98	2.22
High Solvency Petroleum Naphtha ("Amsco Sov A," 219-278°F)	0.92	2.28
VM&P Naphtha (207-293°F)	0.81	2.16
Mineral Spirits No. 10-310-385°F)	0.81	2.22
Benzene	1.16	2.22
Toluene	1.05	2.37
Xylene	0.89	2.32
Methanol	6.08	4.77
Ethanol	3.16	3.56
Isopropanol	1.82	2.68
n-Butyl Alcohol	1.63	2.96
Methyl Acetate	2.90	5.27
Ethyl Acetate	2.05	4.42
Isopropyl Acetate	1.78	4.56
n-Butyl Acetate	1.59	4.52
"CELLOSOLVE" Acetate	1.57	5.08
Acetone	2.50	3.54
Methyl Ethyl Ketone	1.75	3.09
Methyl Isobutyl Ketone	1.35	3.31
Ethyl Ether	1.47	2.67
Carbon Disulfide	1.08	2.01

The LEL concentration of a solvent mixture in air can be determined from the LEL data for the individual components and their weight percentages in the mixture in accordance with the preceding formula.

Materials of Construction

For the recovery of most hydrocarbons, a solvent recovery system can be fabricated from carbon steel. It is, however, important that the support for the carbon itself be of stainless steel as there is a tendency for corrosion to occur where the carbon is in contact with its supporting perforated plate. Chlorinated hydrocarbons hydrolyze during the desorption cycle in the presence of hot, wet steam and activated carbon. When this is encountered, monel is often used in the areas of the solvent recovery system which will be exposed to the hot, wet steam and solvent. In some cases, monel is not adequate and titanium must be used. When ketones such as MIBK, MEK and acetone are being desorbed stainless steel is required.

Because of the greater costs of using alloys in a solvent recovery system, it is wise to review the solvents being used in a process to determine if they are really necessary, or if they can be substituted with a solvent that will not require alloy materials in the recovery system. Even trace amounts of chlorinated hydrocarbons, ketones /acetones, acetic acid or bromine, to name a few, will cause serious corrosion in carbon steel solvent recovery systems. For this reason it is important that complete information be provided to the designer of solvent recovery equipment, so that he may properly specify the system. Often the complete analysis of a coating, resin, ink, etc., is unknown to the user. It is very important that ingredients of his materials be identified.

It is also important that the designer of the solvent recovery system know if ovens, or dryers, are direct fired or use indirect heat exchange. Carbonic acid can be developed within a recovery system from direct fired drying equipment. This does not always happen, but it should be studied.

Sizing of Solvent Recovery Equipment

The total maximum volume of solvent laden air to be received by the solvent recovery system determines its size. The reason for this is that for the carbon to perform satisfactorily the velocity of solvent laden air through the bed should be about 80 fpm. Under some circumstances, sound process design can be achieved at about 100 fpm. It is apparent that the air volume determines the surface of the carbon bed and this in

turn determines the length and diameter of the adsorber vessel. The depth of the carbon bed is mainly established by the quantity of solvent in the incoming solvent laden air stream. Other considerations relating to the bed depth are the establishment of the proper number of mass transfer zones and the determining of an adsorption and desorption cycle which will keep the steam consumption at an acceptable level. Approximately one-half of the total steam used in a desorption cycle is wasted on the sensible heat requirement of the steel and carbon. When the carbon bed is thick enough to provide for a lengthy adsorption cycle and the associated less frequent desorption cycle, less steam will be used over all, i.e., the ratio of steam to recovered solvent will be favorable.

For solvent recovery units up to and including a capacity of 10,000 cfm, it is possible to skid mount and pre-assemble the equipment. Where air volumes greater than 10,000 cfm must be processed, the solvent recovery equipment will be field erected.

Cost of Solvent Recovery Equipment

The cost of solvent recovery equipment varies widely and it is not a straight line function of the cfm. It is generally true that the larger the solvent recovery unit the less cost per cfm. The cost per cfm can range from less than \$5.00 for carbon steel solvent recovery equipment to more than \$25.00 when alloys are used. If equipment must be made of stainless steel components, a multiplier of 1.5 must be applied to the carbon steel price. If the equipment must be fabricated of monel components, a multiplier of 1.9 must be applied to the carbon steel price. Equipment is usually quoted f.o.b. shipping point and for the items described previously under Solvent Recovery Equipment. The cost of freight on the equipment is seldom greater than 3%. The cost of installing the equipment is difficult to quote until such a time that the solvent recovery system is designed, specified, and a layout has been prepared. Even then this will only enable the estimator to quote on the battery limits installation. In addition, the following items will have to be designed and/or specified before a complete in-place cost can be developed:

Ducting and duct support - between source of solvent laden air and the solvent recovery plant.

Piping for the cooling water loop and pumps
Cooling tower - if needed.

Steam line and pressure reducing valve
Supports for same.

Boiler - if needed

Condensate return or disposal.

Motor control center and associated buss or conduit. Typically 240/480 volt.

Spaghetti between control panel and solvent recovery plant.

Foundations.

Rigging

Structural steel.

Ladders and platforms.

Lighting, fencing, painting

Insulation, electric cable or steam tracing for winterizing.

Piping and/or pumping of recovered solvent to storage tanks.

Supply of 110 volt lighting and utility circuit and a welding circuit to the site of the recovery plant

A water line or fire line to the site of recovery plant.

Compressed air to the site of the recovery plant.

These are some of the many things which enter into the final in-place cost of a solvent recovery system. In the past twelve months it has been demonstrated several times that the cost of carbon steel solvent recovery equipment as indicated herein, should be doubled to represent the in-place cost of this equipment, ready to operate.

Utilities

The following are needed to operate a solvent recovery system. Electricity, steam, cooling water, instrument air. In the attempt to estimate utilities, rules of thumb can be misleading. We might be close using an estimate of 7 hp per 1000 acfm of solvent laden air at 100°F. The ratio of steam to solvent can be estimated by using 3.5 lbs. of steam to 1.0 lb. of recovered solvent. However, depending on the nature of the solvent, the steam ratio can go as low as 2 lbs. per 1.0 lb. of recovered solvent, or as high as 9 or 10 lbs. per 1.0 lb. of recovered solvent. The cooling water, of course, depends on the temperature of the solvent laden air stream and the amount of steam used for the desorption cycle.

Below is a tabulation of the utility requirements of various solvent recovery systems. They may be helpful in developing guide lines.

CAPACITIES AND UTILITIES

ACFM	SLA TEMP.	SOLVENT	LB/HR	ELECTRICAL KW	STEAM LB/HR	COOLING WATER GPM
10,000	95°F	Acetone	950	75	2,200	420
10,000	130°F	Toluene & Methanol	280 60	80	1,150	400
60,000	300°F	Toluene Ethanol	2,000 200	210	6,000	1,300
100,000	130°F	Toluene & Mxd. H.C.'s	1,200	510	5,200	1,050
85,000	105°F	Toluene	1,600	400	4,800	500
120,000	115°F	Toluene & Xylene	3,000	350	10,750	1,160
20,000	180°F	Methanol	680	100	2,580	270
24,000	100°F	Acetone	1,600	65	4,710	520
30,000	200°F	Toluene & Misc.	1,500	130	3,800	825
75,000	100°F	Xylene	2,600	225	6,360	700
60,000	150°F	Toluene	2,600	245	5,000	1,100

Safety

Solvent recovery systems are not generally considered to be hazardous. They have been installed outside buildings, inside buildings, or on the roof of buildings. Insurance companies are familiar with this equipment and with the exception of minor details pertinent to a given installation, they generally accept the equipment as designed. When recovering ketones / acetones, there is a possibility of fire occurring if operating instructions are not followed to the letter. When these solvents are adsorbed for a long period of time, or at a very low humidity, a bed fire is almost assured. This condition would be detected and an alarm sounded. If action is taken in a reasonable length of time, no serious damage will be done to the equipment. The system should be steamed immediately to remove oxygen from the vessel and this should be followed by flooding the vessel to cool it, and assure the quenching of the fire.

When it is necessary to enter an adsorber vessel, air packs should be used as the carbon will remove most of the oxygen from the air inside the vessel. Under no circumstances should welding be done in an adsorber vessel without first removing the carbon and thoroughly purging the vessel. We know of no incident where serious damage, or for that matter, even minor damage, has been caused by a solvent recovery system. The equipment is automatic requiring no operator, however, there should be personnel on the premises who can respond to alarms and correct, or adjust, conditions when necessary. When these alarms sound they do not represent an emergency situation.

CONCLUSION

The recycling of solvent "broke" is quite common. It is being done in many hundreds of plants in the United States and hundreds more abroad. We are certain that the owners of many of these plants do not realize they are recovering "broke." They think of it merely as solvent. In any event, they are enjoying the economies of using "broke".

Until recently we have assumed that a very good payout on this equipment would be realized if the solvent laden air to the adsorber was in the range of 25% to 40% of the LEL. Now in a short period of time solvent prices in some cases have tripled, and solvent laden air streams in the range of 10% of the LEL are beginning to look attractive for reasonably fast payout. Some of the solvent recovery plants we have installed to recover high priced solvents such as THF or Freon, have had a payout of between 1 and 2 years. We have installed plants at paper mills and paper converting plants with payouts of about 2-1/2 years. Another way to view the economics of solvent recovery is return on investment. At the present high cost of solvents you may get a greater R.O.I. recovering expensive solvents than if the same money were spent installing a new production line. As a collateral benefit, solvent recovery is indeed a solution to pollution with removal efficiencies in excess of 95%.

When solvent recovery equipment is being considered for your use, it is important that it be thought of as process equipment, not a "black box" to be plugged in like a refrigerator. A solvent recovery plant properly specified and designed for your needs will give very reliable on-stream service, low maintenance, and a favorable utilities cost. Solvent recovery has proven itself over the past 40 years many times over. Perhaps it can recover "broke" for you.