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**“DECOLORACIÓN DE JARABE SIMPLE PARA LA
FABRICACION DE GASEOSAS UTILIZANDO RESINAS DE
INTERCAMBIO IONICO”**

INFORME DE SUFICIENCIA

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RESUMEN

La producción de bebidas gaseosas se realiza con la mezcla del jarabe simple y concentrado, donde el Jarabe simple, que es la mezcla de agua y azúcar a una determinada concentración (°Brix), no debe presentar coloración visible y llegar a un determinado grado de color (ICUMSA).

Para lograr que el jarabe simple tenga el grado de color deseado, es necesario realizar el proceso de decoloración, que convencionalmente es logrado por medio de la filtración en caliente con carbón activado, sin embargo con el desarrollo de nuevas tecnologías, hay nuevos métodos para lograr este proceso.

El objetivo del presente informe es el de describir el uso de resinas de intercambio iónico para la decoloración del jarabe simple y presentarlo como una alternativa para reemplazar o añadirlo a la tecnología ya existente.

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I. INTRODUCCION

En el proceso de fabricación de gaseosas existe una etapa que consiste en la preparación por lotes de solución azucarada (agua tratada y azúcar refinada) – jarabe simple.

El agua tratada proviene de la planta de tratamiento de la embotelladora y el azúcar de la empresa que provee este insumo (ingenio). Esta solución es preparada en un tanque y presenta ciertos parámetros: °Brix, color, temperatura, viscosidad, normalmente esta solución presenta un color oscuro producto de las impurezas del azúcar refinada por lo que es necesario realizar una filtración por batch de esta solución, para lo cual se utiliza carbón activado en polvo y un filtro prensa para remover las partículas finas en suspensión. El proceso de filtración se realiza en caliente y por lotes. Actualmente en otros países como Estados Unidos, Brasil, Argentina, vienen utilizando resinas de intercambio iónico para conseguir esta “purificación” o reducción del color.

Las ventajas de esta tecnología frente a la existente son:

1. Proceso continuo;
2. Las resinas se pueden regenerar y volver a utilizar, mientras que el carbón activado no;
3. Mayor producción de lotes de filtración o jarabe filtrado comparado con el sistema actual;

1.1 OBJETIVO

- Difundir la tecnología del uso de resinas de intercambio iónico para la decoloración de soluciones azucaradas.
- Presentar la aplicación de la tecnología en el rubro de fabricación de gaseosas.

II. DESARROLLOS Y CONCEPTOS DEL TEMA

Son varios los ejes a tener en cuenta dentro del proceso de fabricación de las gaseosas. En principio hay que contemplar las condiciones mínimas que debe tener una planta embotelladora para poder envasar bebidas gaseosas.

En ese sentido los diversos componentes deben estudiarse puntualmente:

2.1. AGUA:

Compone aproximadamente el 85-90% del producto y deberá cumplir con lo siguiente:

2.1.1. Características Físico-Químicas (*Ver TABLA 1.*)

Potable	Incolora - Insípida - No Contaminada
Sedimentos	0 TDS
Turbidez	0 NTU
Sólidos Totales	500 mg/L Máximo
Alcalinidad Total	60 mgmg/L Máximo
Dureza Total	100 mg/L Máximo
Cloruros	200 mg/L
Sulfatos	200 mg/L
Hierro	0.3 mg/L Máximo
Nitritos	0 mg/L
Cloro	0 mg/L
Manganeso	0 mg/L

TABLA 1. CARACTERÍSTICAS FÍSICO-QUÍMICA DEL AGUA

2.1.2. Condiciones Microbiológicas (Ver TABLA 2.)

Bacterias totales	200 UFC/ml. Máximo
Grupo coliformes	Ausente / 100 UFC/ml.
Pseudomonas aeruginosas	Ausente / 100 UFC/ml.

TABLA 2. CONDICIONES MICROBIOLÓGICAS DEL AGUA

Es fundamental que no se utilice agua ozonizada en la elaboración de refrescos.

2.2. AZÚCARES:

- Calidad: blanca, refinada de primera calidad (sacarosa 99,5% en peso)
- Olor, color y sabor característicos.
- Un jarabe al 50% (azúcar y agua) acidificado a pH 1,5 con ácido fosfórico, no deberá desprender olores extraños.
- Una dilución a 15° Brix y calentada a 50° C no deberá tener olor ni sabor a melaza ni otros olores o sabores extraños.

2.3. MATERIAS PRIMAS

La calidad de la materia prima en la elaboración de bebidas gaseosas deberá ser grado alimenticio (FDA) / farmacéutico (U.S.P.) adecuadas a lo requerido en las fórmulas correspondientes y autorizados por los Reglamentos Alimentarios Nacionales. La calidad de origen, debe ser mantenida durante su almacenamiento y manipuleo (humedad, temperatura, contaminaciones, etc.) Las características de las materias primas a utilizar deberán estar claramente especificadas en las fórmulas (pureza, concentraciones, grados de humedad, etc.). Es conveniente contar con “Certificados de Calidad” del proveedor / exportador. Toda materia prima debe tener sus envases originales, cierres de seguridad y estar perfectamente rotuladas.

2.4. FORMULACIONES

Disponer de recetas claras, precisas, indicando cantidades exactas, unidades de medida (peso/volumen), especificaciones de los ingredientes con orígenes recomendados, código de identificación del proveedor, etc.

2.5. PROCESOS PARA LA ELABORACION DE LAS BEBIDAS GASEOSAS

El proceso productivo para la bebida gaseosa, consta de una serie de etapas (*ver Apéndice I*). El proceso inicia con la obtención de agua, extraída de un pozo propio, que luego de pasar por procesos de purificación, filtrado en arena y filtrado en carbón activado; son mezclados con azúcar para obtener el jarabe simple al que se le agregan preservantes, concentrados, etc., y se obtiene el jarabe terminado.

Luego el jarabe terminado es enfriado y mezclado con agua y CO₂ para ser embotellado.

2.5.1. PROCESO DE ELABORACION DEL JARABE SIMPLE

La elaboración del jarabe simple se realiza mediante las siguientes etapas (*ver Apéndice II*):

2.5.1.1. Mezclador.

En un tanque de capacidad de 1500 galones se adiciona Azúcar (4000 kg), agua tratada (1400 L), tierra de Diatomea (6 kg a 8 kg dependiendo del tipo de azúcar) y carbón activado (3 kg a 6 kg). Este tanque tiene un agitador en la parte inferior con un motor que sirve para que todo el azúcar sea disuelto totalmente y se Pasteuriza a una temperatura de 80°C, dando lugar al jarabe simple

2.5.1.2. Reposo

El jarabe simple obtenido del mezclador es llevado a un Tanque de Acero Inoxidable enchaquetado de capacidad de 2000 gal. para su reposo durante 30 minutos.

2.5.1.3. Filtración I.

Luego de haber reposado, al jarabe se hace recircular entre el Tanque de Acero Inoxidable con una marmita hasta que el jarabe esté claro con una turbidez menor a 3 NTU y no haya presencia de carbón, esto se logra en un promedio de 1 ½ hora.

La marmita consta de 9 placas, en las cuales hay una formación de Pre-capa homogénea de Tierra de Diatomea que es formada a partir de una solución de agua tratada y 11 kg de tierra. Esto actúa como un filtro para que el carbón y la tierra adicionada en el tanque se compacten con la pre-capa.

La temperatura, luego de los dos procesos anteriores, desciende de 80°C a 60°C en promedio.

2.5.1.4. Enfriamiento

El jarabe simple claro y exento de sabores y olores extraños gracias al carbón y a la tierra es enfriado mediante un Intercambiador de Calor de Placas. La temperatura del jarabe simple desciende de 60°C a 22°C, el fluido utilizado para el enfriamiento es agua helada.

2.5.1.5. Filtración II.

El jarabe ya enfriado es enviado mediante un filtro manga de 1µm hacia la línea de jarabe terminado; este filtro retiene cualquier impureza que no haya sido retenida por el filtro de placas.

2.6. CONTROL DE CALIDAD

Existen controles de calidad que deben llevarse a cabo durante el proceso de elaboración de jarabe simple:

- (a) Grados Brix - Método: Refractométrico / densimetría;
- (b) Verificación del contenido de azúcar (tablas de sacarimetría – grados Brix / litros de jarabe simple)

III. DESARROLLO DEL TEMA

El jarabe simple requerido para la elaboración de las bebidas gaseosas debe ser menor a 50 ICUMSA, para esto hay procesos tradicionales, como el usado con carbón activado mencionado en el capítulo anterior. Sin embargo, el tratamiento con resinas de intercambio iónico, han venido ganado terreno en los últimos tiempos. En un inicio, el objetivo del uso de estas resinas era para reducir el contenido de cationes e incrementar el rendimiento del agua. El desarrollo de la tecnología de resinas de intercambio iónico, mucho más eficientes, basadas en copolímeros de estireno/divinilbenceno enlazado con poliacrilamidas, algunas de las cuales tienen estructuras macroporosas, han considerablemente incrementado tanto el rendimiento como la pureza de los productos finales [3].

Además de la desmineralización y decoloración de jarabes de baja viscosidad, están ganando importancia, técnicas cromatográficas, procesos de exclusión iónica, decoloración de jarabes de alta viscosidad y la producción de soluciones de azúcar líquido.

En la actualidad, los principales campos de resinas de intercambio iónico en la industria azucarera pueden ser descritos como sigue:

- Decoloración
- Desmineralización
- Inversión Controlada
- Exclusión de Iones
- Substitución selectiva de iones

3.1. FORMACION DEL COLOR Y TIPO DE COLOR

La apariencia o color del jarabe simple puede variar desde el amarillo claro hasta un intenso rojo caoba [1].

Existen varios tipos de color (llamado así en la industria azucarera) o colorante (*Ver TABLA N°3*).

TIPOS DE COLOR	CARACTERÍSTICAS
Pigmentos vegetales	Provenientes de la caña de azúcar
<u>Melanoides</u>	Las reacciones de aminoácidos y azúcares reductores que forman la <u>melanoidina</u> por la reacción de <u>Maillard</u>
Caramelo	Las reacciones de degradación y condensación térmicas de los azúcares que forman el caramelo
Productos de degradación alcalinas	La reacción alcalina de la degradación y condensación de los azúcares. Similares al caramelo, pero más oscuro y formado a PH altos
Fenólicos	El oscurecimiento enzimático es la reacción oxidativa de los compuestos polifenólicos. Los fenoles oxidadas incluyen todas las enzimas capaces de catalizar la <u>hidroxilación</u> de los <u>monofenoles</u> a <u>difenoles</u> y la oxidación posterior de los <u>difenoles</u> a quinonas. El paso fundamental en la secuencia de reacción que conduce a la formación de color es la oxidación del <u>O-difenol</u> a la <u>quinona</u> .

TABLA 3. TIPOS DE COLOR Y SUS CARÁCTERÍSTICAS [1]

Es económicamente imposible instalar un sistema que decolore todos los tipos de colorantes. Es esencial en la práctica, con fines de diseño, clasificar los colorantes en las siguientes categorías [1]:

Tipo I. Iónicos/aromáticos

Este grupo de colorantes tienen un grupo funcional y una estructura aromática básica como parte de la estructura molecular (*Ver Figural*). Este tipo puede

básica como parte de la estructura molecular (*Ver Figura1*). Este tipo puede removerse mediante un adsorbente ya sea con función de intercambio de iones y/o superficies aromáticas.

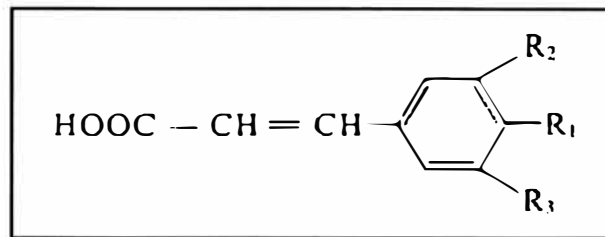


FIGURA 1. COLORANTE DEL TIPO I, IÓNICO/AROMÁTICO

Tipo II. No iónicos/aromáticos

Esta presencia es por naturaleza altamente aromática (*Ver Figura2*). Ningún grupo iónico está presente. Este tipo de colorante se remueve de la manera más efectiva mediante resina Poliestirénicas.

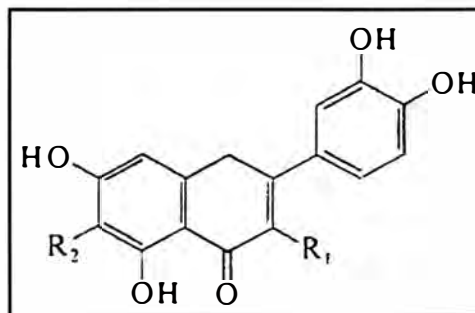


FIGURA 2. COLORANTE DEL TIPO II, NO IÓNICO/AROMÁTICO

Tipo III. Iónicos/No aromáticos

Este grupo contiene grupos iónicos funcionales con estructura molecular alifática muy probablemente con dobles enlaces conjugados (*Ver Figura3*). Debido a su naturaleza alifática, este grupo se elimina de manera efectiva mediante un mecanismo de intercambio de iones y en cierto grado, por precipitación. Si el

doble enlace se conjuga ampliamente, también se puede adsorber por medio de adsorbentes aromáticos.

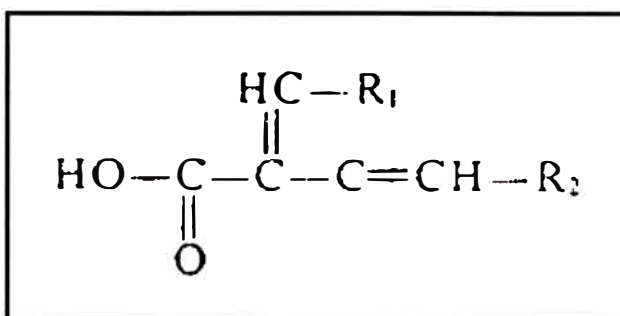


FIGURA 2. COLORANTE DEL TIPO II, NO IÓNICO/AROMÁTICO

Tipo IV. No iónicos/No aromáticos.

Este grupo constituye un pequeño número de colorantes que son muy difíciles de remover los adsorbentes de que se dispone usualmente, a menos que la fracción aromática esté altamente conjugada.

3.2. MECANISMOS DE DECOLORACIÓN.

La remoción de los colorantes por lo general resulta de uno o la combinación de los tres mecanismos siguientes [1]:

- 1) *Adsorción mediante enlaces hidrofóbicos*, por ejemplo la remoción de un colorante por carbón.
- 2) *Intercambio de iones por medio de un grupo iónico funcional*, por ejemplo, los colorantes iónicos removidos por resinas de intercambio iónico.
- 3) *Precipitación* seguida por oclusión y/o adsorción de fuerzas de Van Der Waals

Los tipos de mecanismos mencionados se resumen como sigue:

1. **Intercambio iónico:** colorantes ácidos retenidos por resinas en forma aniónica
2. **Adsorción:** Enlaces hidrofóbicos (interacción aromático-aromático).
3. **Precipitación:** se forman complejos con sustancias orgánicas como sales de amonio cuaternario/cationes inorgánicos como Ca^{2+} .
4. **Absorción:** atrapado dentro del cristal/adsorbente poroso.
5. Combinación de los anteriores.

3.3. TIPOS DE AGENTES DECOLORANTES

Una vez conocido tanto la naturaleza de los colorantes como el mecanismo de la remoción del color, la siguiente tarea es seleccionar el agente o agentes decolorantes comercialmente obtenibles a fin de maximizar la eficiencia decolorante con el mínimo de capital y costos de operación. Los siguientes agentes son los que se utilizan con mayor frecuencia [1]:

1. Resinas de intercambio iónico

Resinas Poliestirénicas

A causa de la naturaleza aromática de la estructura del anillo bencénico, este puede remover los colorantes por la vía tanto del mecanismo de adsorción como de intercambio de iones (*Ver Figura 4*).

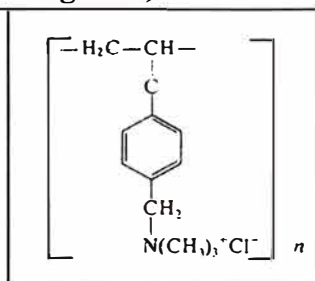


FIGURA 4. RESINA DE INTERCAMBIO POLIESTIRÉNICA

Resinas Poliacrílicas

La adsorción por esta resina de tipo alifático de elevado peso molecular resulta mínima (*Ver Figura5*). La remoción de color se efectúa por la vía del proceso de intercambio de iones. Por consiguiente, este tipo está menos sujeto a ensuciamiento.

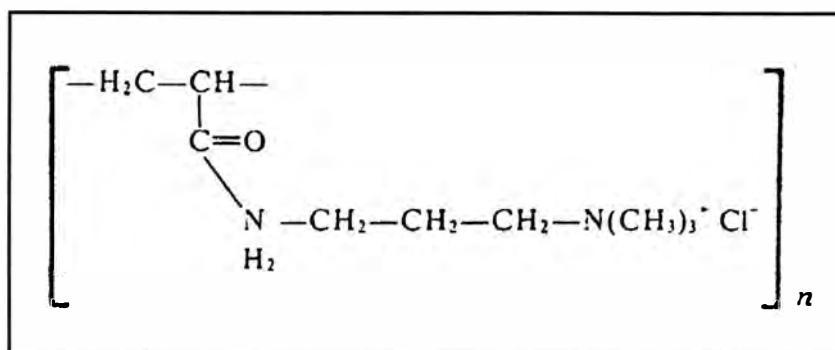


FIGURA 5. RESINAS INTERCAMBIO IÓNICO – POLIACRÍLICAS

2. Carbón granulado y pulverizado

Este grupo es el mejor agente para la adsorción de los colorantes de naturaleza aromática y con dobles enlaces conjugados. Asimismo, se remueven colorantes de elevado peso molecular, particularmente los de tipo de ácido débil.

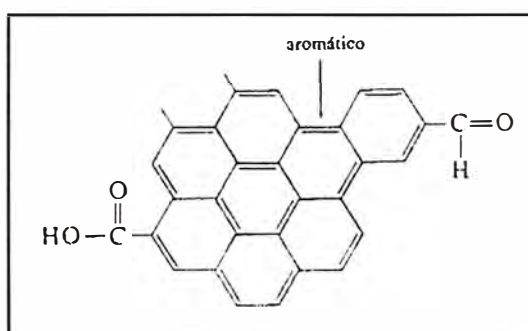


FIGURA 6. ESTRUCTURA CARBÓN GRANULADO

3. Carbón Animal. Además de la remoción de color por la porción carbónica del carbón de hueso que se acaba de describir, la hidroxiapatita puede también

adsorber colorantes. Esto es particularmente notable cuando los colorantes iónicos son precipitados por el calcio presente en el carbón animal.

4. **Carbonatación.** Es de esperar que el mecanismo de remoción del color se ajuste a la teoría de precipitación seguida por adsorción (oclusión). Asimismo, es posible la adsorción de coloración de muy alto peso molecular.

5. **Fosfatación** con o sin sales de amonio cuaternario. La remoción del color se realiza en su mayor parte por precipitación seguida de absorción/adsorción. El uso de las sales de amonio cuaternario es más efectivo cuando están presentes colorantes altamente ácidos.

3.4. TECNOLOGIA DEL PROCESO

Nosotros nos enfocaremos, básicamente, al mecanismo de intercambio de iones o mejor dicho, decoloración usando resinas de intercambio iónico. Una de las razones principales por la que este mecanismo se usa cada vez con más frecuencia es que no es necesario utilizar calor en la regeneración, ahorrando el consumo de energía. La única desventaja de este método es la eliminación del regenerante.

3.4.1. DESCRIPCION DE LOS INTERCAMBIADORES DE IONES

Los intercambiadores de iones son materiales insolubles que poseen sitios iónicos. Muchos materiales muestran una cierta capacidad de intercambio, pero para que un intercambiador de iones sea útil es necesario que haya un gran número de sitios de intercambio. El grupo iónico, normalmente soluble, se hace insoluble fijándolo a un polímero, o resina; de aquí que los a los intercambiadores de iones se les llame frecuentemente resinas de intercambio iónico.

Los intercambiadores de cationes: se pueden considerar como aniones insolubles, en los que el catión acompañante se intercambia con facilidad. Sus grupos

funcionales son los ácidos sulfónico, carboxílico, o fosfórico.

Los intercambiadores de aniones: se pueden considerar como cationes insolubles, en lo que los aniones acompañantes se intercambian con facilidad. Su grupo funcional son las aminas cuaternarias, terciarias o secundarias.

Las resinas que más se emplean como soporte son el estireno enlazado en forma transversal con el divinil benceno, o los polímeros acrílicos. Como tales, son productos derivados del petróleo, y sus costos están estrechamente relacionados con el precio del petróleo. Las resinas de intercambio de iones tienen por lo general la forma de cuentas porosas.

El proceso de intercambio de iones es muy rápido, por lo que sólo se requiere un tiempo de contacto de unos pocos minutos. La profundidad de los lechos es pequeña, solo unos cuantos pies, por consiguiente el tamaño del equipo no es muy grande comparando con lo usado con los adsorbentes de carbón. El volumen del jarabe simple retenido en los lechos de resina es pequeño y el tiempo de retraso en el proceso es corto.

3.4.2. RESINAS DE INTERCAMBIO IONICO USADAS PARA LA DECOLORACION

Las resinas de intercambio las cuales están acondicionadas para remover el color deben tener las siguientes características [1]:

- Resinas de intercambio aniónico fuertemente básicas con grupos del tipo amonio cuaternario, trabajando en su forma de cloruro para asegurar que el valor de pH del jarabe simple no sea cambiado.
- Alta macroporosidad, requerido para arreglar colorantes de alto peso

molecular por adsorción.

- Alta resistencia al shock osmótico, por lo que la resina pueda resistir los cambios repentinos de la concentración entre las etapas de regeneración y desendulzado.
- Especial tamaño de partícula. Finas esferas, la combinación con la alta viscosidad de la solución azucarada podría causar alta pérdida de presión. Las esferas comunes (tipo gel) tienen menos capacidad de adsorción.

Las resinas de amonio cuaternario fuertemente básicas se operan en ciclo cloruro. En la operación, el cloruro se intercambia por el anión colorante. Asimismo, se presenta una considerable adsorción del colorante del azúcar en la matriz de la resina. La regeneración se lleva a cabo con salmuera. La forma física de la resina que se prefiere es la macrorreticular debido a que es de naturaleza porosa más abierta, lo que permite que las grandes moléculas del colorante alcancen más fácilmente los sitios de intercambio o adsorción. Además es ensuciada menos por los compuestos fenólicos.

Las resinas acrílicas son más resistentes, duran más tiempo, pero tienen más baja capacidad para el colorante del azúcar. En la actualidad se observa una tendencia a utilizar resinas tanto acrílicas como estirénicas en serie, con la resina acrílica en primer lugar a fin de tomar la mayor parte de carga de fenoles. Las resinas acrílicas pueden efectuar mejor lo anterior y se regeneran de una manera más limpia de sobrecarga. Las resinas de estireno son de mayor capacidad, remueven los colorantes hasta un nivel más bajo. La mejor decoloración tiene lugar a un pH

por encima de ocho en el que los colorantes están altamente ionizados.

En la regeneración, se ha encontrado que parte de los cuerpos de color removidos del jarabe simple por la resina aniónica no se separan totalmente de la resina por el simple tratamiento con salmuera. Algunos investigadores han encontrado que la salmuera alcalina resulta beneficiosa.

Bayer AG [2] tiene desarrollado diferentes resinas de intercambio iónico, las cuales son usadas para la decoloración de soluciones azucaradas.

En este informe se hace mención a dos resinas Lewatit que son la S 6368 y VP OC 1074, ambas son resinas aniónicas de base fuerte. En la Tabla 2 se detalla las características de ambas resinas.

LEWATIT, TIPO		RESINAS DE INTERCAMBIO ANIONICO FUERTEMENTE BASICAS	
		S 6368	VP OC 1074
DESCRIPCION DEL PRODUCTO			
Forma Suministrada		Cloruro	Cloruro
Grupo Funcional		Amina cuaternaria	Amina cuaternaria
Matriz		Poliestireno entrecruzado	Poliacrilamida entrecruzada
Estructura		Macroporosa	Macroporosa
Apariencia		Beige opaco	Bianco opaco
DATOS DEL PRODUCTO			
Rango de Tamaño, min 90%	mm	0.63 (± 0.05)	0.4-1.6
Tamaño efectivo	mm		0.55 (± 0.05)
Coefficiente de Uniformidad	max	monodisperso	1.8
Densidad aparente ($\pm 5\%$)	g/l	670	680
Densidad	aprox. g/l	1.08	1.08
Contenido de agua	%	50-60	66-72
Capacidad total	mln. eq/l	1.1	0.85
ESTABILIDAD			
	a Temp. °C	<85	<75
	en rango pH	0-14	0-14
VIDA UTIL			
	min. años	2	2
	a Temp. °C	-20 a 40	1 - 40

TABLA 4. CARACTERÍSTICAS DE LAS RESINAS S6368 Y VP OC 1074

3.4.3. DESCRIPCION DEL PROCESO DE DECOLORACIÓN CON RESINAS DE INTERCAMBIO IONICO

El óptimo proceso para el tratamiento de decoloración del jarabe simple es el lecho fluidizado. La alta densidad de las soluciones azucaradas hace ideal el flujo ascendente en el cual la mayoría de resinas flotan libremente en la unidad de intercambio esto previene la formación de capas de lecho de resina mientras se asegura una baja fuga de cuerpos de color y bajo exceso de químicos regenerantes.

La resina de intercambio iónico es colocada entre el plato de toberas en unidades de una o más cámaras. Como la solución a ser tratada fluye hacia arriba de la unidad, esta presiona a la resina de intercambio contra el plato de toberas o difusores. Una capa de material inerte, LEWATIT IN 42, previene la colmatación de las toberas. Las unidades son regeneradas en forma descendente en contra-corriente al modo de operación (*Ver Figura7*). Las toberas y el material inerte aseguran la óptima distribución del regenerante. Las dos fases no se mezclan durante la etapa de desendulzado porque el licor con más alto peso específico está siempre por debajo de la fase acuosa.

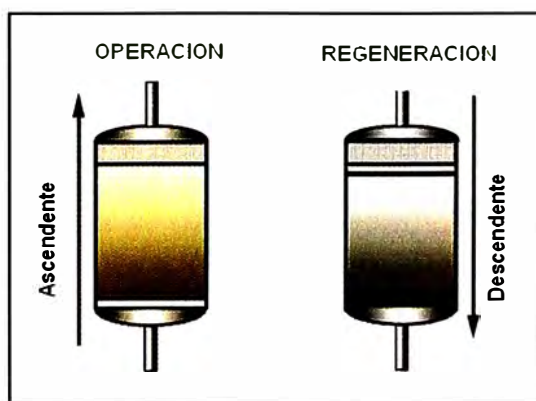


FIGURA 7. PRINCIPIO BÁSICO DE OPERACIÓN DE LAS RESINAS LEWATTIT [3]

La secuencia típica de operación de una unidad aniónica de decoloración es:

1. Endulzado
2. Servicio u operación
3. Desendulzado
4. Lavado en contracorriente
5. Regeneración por salmuera.
6. Desplazamiento de la Salmuera
7. Enjuague final

Si una columna decolorante va estar sin trabajar, por ejemplo, durante un fin de semana, la secuencia anterior se puede interrumpir entre las etapas 5 y 6, lo que permite que la resina quede en la salmuera durante la parada.

3.5. ARREGLO DE LAS RESINAS LEWATIT

Una, dos o tres etapas de proceso son usados, dependiendo de la concentración de los cuerpos de color en el licor. La resina LEWATIT OC 1074 de base poliacrilato o la resina LEWATIT S6368, de base poliestireno, o la combinación de estas dos, proveen mayor efectividad con las soluciones de caña de azúcar, las cuales tienen un alto contenido de cuerpos de color.

Los resultados de la decoloración pueden ser siempre mejorados si dos o tres columnas son usadas en serie. La primera resina provee una principal limpieza mientras que la segunda resina sirve como un pulidor. Las columnas son regeneradas en serie comenzando con el pulidor. Como el pulidor tiene menos materia colorante retenida que la primera columna, su ciclo de operación es más

prolongado.

La recomendación del fabricante de resinas LEWATIT para la decoloración de soluciones azucaradas provenientes de la caña de azúcar está en función a la medida de color en la alimentación (*ver Tabla 5*).

COLOR DE LA ALIMENTACIÓN	CÓDIGO DE RESINA
30 – 200 ICUMSA	S 6368
200 – 600 ICUMSA	OC 1074 – S 6368
600 – 1200 ICUMSA	OC 1074 – OC 1074 – S 6368

TABLA 5. TIPOS DE RESINA LEWATIT A USAR DE ACUERDO A LA MEDIDNA DE COLOR DE LA ALIMENTACIÓN [3]

De acuerdo a las características del jarabe simple que se tiene, el color de la alimentación es de 280 ICUMSA por lo que usaríamos primero la resina OC 1074 y luego la resina S6368 para nuestra prueba experimental.

3.6. VIDA DE LA RESINA

La adsorción de los cuerpos de color y el tiempo de servicio de la resina adsorbadora depende de una variedad de factores incluyendo:

- pH
- Temperatura
- Contenido de electrolito en solución
- Tipo y concentración de los cuerpos de color

Se espera que la resina adsorbadora usada para la decoloración de soluciones azucaradas trabaje en condiciones difíciles. La resina de intercambio iónico

frecuentemente se somete a choques osmóticos cuando cambian de jugos azucarados concentrados a agua, durante el ciclo de desendulzado y a altas concentraciones de soluciones de salmuera durante la regeneración. El ensuciamiento orgánico causado por la alta cantidad de color de la solución azucarada resulta también en un progresivo declinamiento en el porcentaje de decoloración (*Ver Figura 8*).

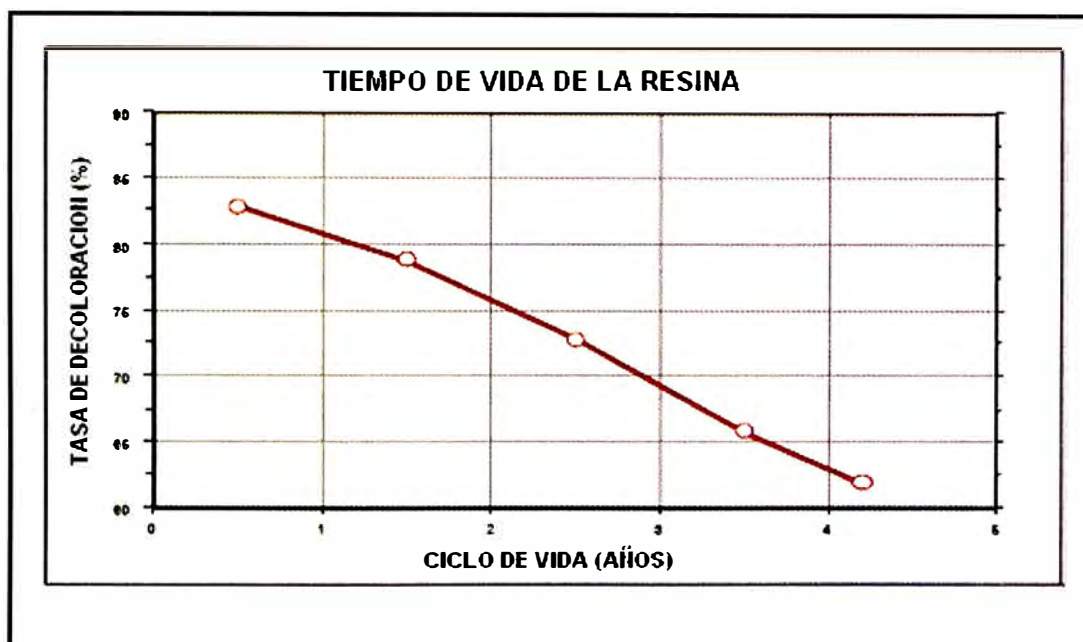


FIGURA 8. EJEMPLO DE VIDA DE LA RESINA LEWATIT S6368 EN UNA REFINERIA DE AZUCAR [3]

Cuando se trabaja con resinas adsorbedoras es aconsejable remover sustancias que bloquean con oxidantes tales como Hipoclorito de Sodio (NaOCl) aproximadamente una o dos veces al año (no se recomienda en el caso de la resina LEWATIT OC 1074 – S 6368).

La vida de la resina decolorizadora de intercambio iónico depende también de las siguientes propiedades, tales como:

- Tamaño de la esfera;
- Porosidad;
- Tamaño de poro;
- Contenido de agua;
- Tipo de ion opuesto;
- Número de grupos fuertemente básicos;

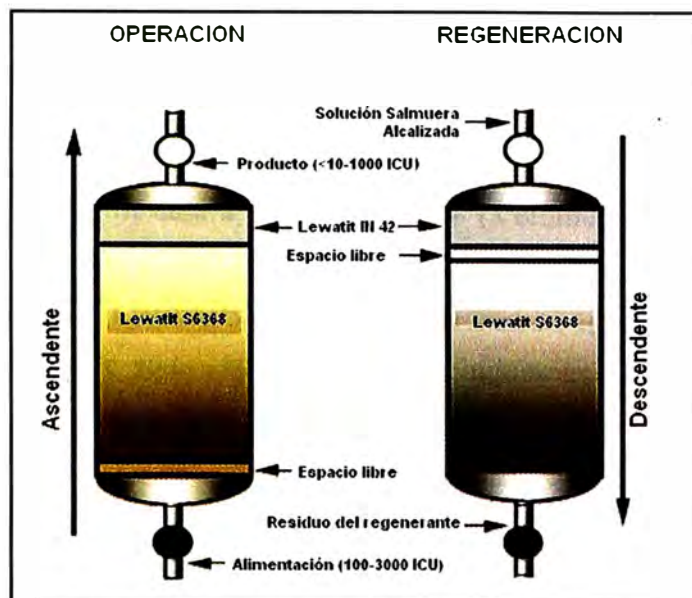
Las resinas normalmente son usadas en su forma de cloruro y regeneradas con una solución de salmuera o una solución alcalizada de un sal común.

3.7. PARÁMETROS DEL PROCESO DE DECOLORACION

La siguiente tabla muestra los datos principales de una planta de operación:

Influente		
Rango de color usual	100-2000 ICUMSA	
Substancia seca	60-75 °BRIX	
Temperatura	60-80 °C	
Caudal	1-4 Volumen de lecho (BV):h	
Regeneración		
Regenerantes químicos	NaCl	NaCl / NaOH
Cantidad de regenerantes	100-200 g/l	100-200 g/l / 5-20 g/l
Concentración de regenerantes	10%	10% / 0.5-1 %
Caudal	1-2 BV/h	1-2 BV/h
Desempeño de las resinas		
Ratio de decolorización	70-95%	
Capacidad	30-350 BV de Jarabe de ingreso	
Vida de resina	Normal	300-500 ciclos
	Posible	100-1000 ciclos

TABLA 6. DATOS PRINCIPALES DE UNA PLANTA DE OPERACION [3]



**FIGURA 9. PROCESO DE DECOLORIZACIÓN LEWATIT –
TECNOLOGÍA DE LECHO FLUIDIZADO[3]**

El rango de coloración de las soluciones azucaradas en su mayoría se encuentran entre 100 y 6000 ICUMSA, alguna veces el color de ingreso a la resina adsorbedora llega a 1000 ICUMSA. Para mayores contenidos de color de 1000 ICUMSA no es recomendable tratar mediante el proceso de resinas de intercambio iónico base fuerte, para esto, se requiere de etapas de limpieza previas tales como carbonatación, tratamiento con sulfito o tratamiento con carbón animal, que son más económicos.

Siempre que el tratamiento sea posible debería involucrar concentraciones sobre 60° Brix y temperaturas alrededor de 60-80°C. El valor de la viscosidad de las soluciones establece el límite para la caída de presión a través del lecho de intercambio iónico.

El caudal está en el orden de 3 BV (Volumen de lecho)/h. Un caudal por encima de este valor daría un bajo porcentaje de remoción de color y podría causar

El caudal está en el orden de 3 BV (Volumen de lecho)/h. Un caudal por encima de este valor daría un bajo porcentaje de remoción de color y podría causar problemas de pérdida de presión.

La regeneración es llevada a cabo con 2 BV (Volumen del lecho) de solución neutra (RESINA ACRILICA) o solución de salmuera alcalizada (RESINA ESTIRENO/DIVINILBENCENO). La concentración química debería ser 10% Salmuera y 1-2% de soda cáustica. Algunas industrias han intentado reducir la cantidad de químicos regenerantes con el fin de ahorrar costos y aguas de desecho. La máxima reducción de químicos es posible utilizando el volumen de la segunda mitad del efluente regenerado como el primero de la primera etapa de regeneración. Por supuesto es necesario el almacenamiento del efluente regenerado. Para la decoloración del efluente regenerado se ha desarrollado el uso de membranas u oxidación química.

El rango de velocidad de decoloración está entre 70% y 95% dependiendo de la concentración del color de la alimentación y el arreglo de la resina. El rango de capacidad de la resina también se encuentra entre 30-350 BV (volumen del lecho) dependiendo también del contenido de color de la alimentación. Para garantizar una vida larga de la resina no se debería sobre cargar con cuerpos de color.

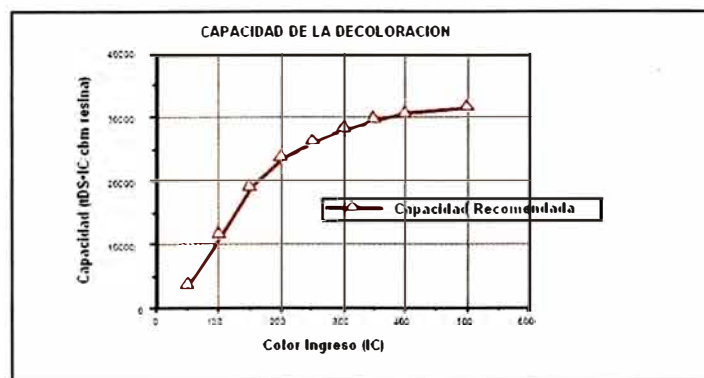


FIGURA 10. REFERENCIA PARA LA MÁXIMA CARGA DE COLOR RECOMENDADA [3]

3.8. SECUENCIA / TIEMPO DEL SISTEMA SUGERIDO

OPERACIÓN	VOLUMEN	CAUDAL (BV)	TIEMPO (BVh)	h
Desendulzado	Agua desmineralizada	15-25	1 - 4	0.5-1
Regeneración	NaCl / NaOH 10% / 2%	2	1-2	1 - 8
Enjuague lento	Agua desmineralizada	1 - 2	1 - 2	1
Enjuague rápido	Agua desmineralizada	1 - 5	1 - 5	1
Endulzado	Jarabe	1.5- 2.0	2- 4	1
Servicio	Jarabe	30 - 300	1 - 4	8 - 150
Temperatura	Servicio y regeneración 60 - 85°C			
Dirección de flujo	Endulzado y Servicio : Ascendente; Todas las otras operaciones: Descendente Desmineralizada, decaionizada o Blanda, condensada			
Calidad del agua				

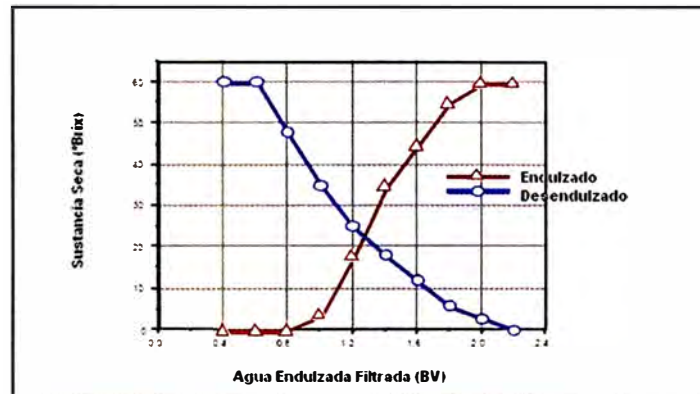
TABLA 7. SECUENCIA/TIEMPO DEL SISTEMA SUGERIDO [3]

Además de la excelente decoloración y baja demanda de químicos regenerantes, el procedimiento de endulzado y desendulzado son de principal interés.

El agua usada para el desendulzado de la columna deberá ser agua desionizada o agua blanda. Para prevenir cualquier pérdida de azúcar y limitar su dilución en la siguiente etapa de operación (Regeneración) se recomienda:

- Llevar el efluente (agua desendulzada concentrada de la etapa de desendulzado) al tanque de jarabe tratado hasta que la concentración del mencionado efluente sea aproximadamente 50° Brix.
- Después que el efluente llegue a 50°Brix, éste es llevado hacia el tanque de agua desendulzada concentrada. El proceso debe ser detenido cuando la concentración del efluente sea aproximadamente 20° Brix.
- Luego que el efluente llega a 20°Brix (ahora llamado agua desendulzada diluida), este se lleva a otro tanque (tanque de agua desendulzada diluida).

- El proceso de desendulzado se detiene cuando la concentración del efluente sea aproximadamente 0.5° Brix.



**FIGURA 11. CURVAS TÍPICAS DE ENDULZAMIENTO –
DESENDULZADO EN UN SISTEMA LEWATIT [3]**

3.9. PROYECCION DEL FABRICANTE PARA EL SISTEMA DE DECOLORACION POR MEDIO DE RESINAS DE INTERCAMBIO IONICO

Se ha efectuado una corrida con el programa del fabricante de resinas LEWATIT (ver *Tabla 8*) con el fin de determinar el volumen de la resina y volumen de la columna, los datos de entrada son:

Sustancia Seca (° Brix)

Temperatura (°C)


Viscosidad (cp.)

Caudal (cbm/h)

Tiempo de servicio (horas)

Color de Ingreso (ICUMSA)

Color deseado – Salida (ICUMSA)



Customer		Embotelladora Don Jorge	
Project		Peru	
System		Lewatit VWS-OC 1074-S 6368	
Requested parameters			
Dry substance	[°Bx]	90.0	
Service time	[h]	12.0	(8 days)
Flow rate (volume) / hour	[cbm/h]	14.8	
Flow rate (metric) / hour	[t/h]	19.1	
Flow rate (ds) / hour	[t ds/h]	11.4	
Throughput (volume) / cycle	[cbm/cycle]	178	
Throughput (mass) / cycle	[t/cycle]	229	
Throughput (ds) / cycle	[t ds/cycle]	137	
Temperature	[°C]	60	
Density	[g/ml]	1.289	
Viscosity	[cp]	10.0	
Colour content			
Feed colour	[cuma]	260	
Colour load / cycle	[ds*colour]	38.487	
Lewatit Resin		OC 1074	5 6368
Resin capacity calculation basis	[ds*colour / cbm]	6.000	
Throughput / cycle	[bed volume]	55	
Resin volume	[litre]	3.206	3.206
Inert resin volume	[litre]	195	195
Regeneration			
NaCl quantity / litre resin	[g/l resin]		200
NaOH quantity / litre resin	[g/l resin]		
NaCl quantity / cycle	[kg 100% / cycle]		1282
NaOH quantity / cycle	[kg 100% / cycle]		0
Unit-Designing			
		down chamber	top chamber
Column diameter	[mm]	1600	1600
Column diameter (internal)	[mm]	1578	1578
Column area (internal)	[qm]	1.95	1.95
Specific flow rate	[bwh]	4.62	4.62
Linear flow rate	[m/h]	7.57	7.57
Resin bed depth	[mm]	1640	1640
Freeboard	[mm]	160	160
Freeboard	[%]	9.8	9.8
Inert resin / bed depth	[mm]	100	100
Cylindrical height	[mm]	1.900	1900
Total cylindrical height	[mm]		3800
Number of nozzles recommended	approx. / plate	117	117
Pressure drop	[kPa]	137	137

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TABLA 8. PROYECCION DEL FABRICANTE PARA EL SISTEMA DE DECOLORACION POR MEDIO DE RESINAS DE INTERCAMBIO IONICO

3.10. DIAGRAMA DEL PROCESO DE DECOLORACIÓN DEL JARABE SIMPLE CON RESINAS DE INTERCAMBIO IONICO

Se ha elaborado un diagrama de proceso de decoloración usando la tecnología de resinas de intercambio (*Ver Apéndice III*).

IV. CONCLUSIONES

1. El desarrollo actual de los fabricantes de resinas de intercambio permiten encontrar resinas para diferentes aplicaciones industriales, éstas tienen diversas propiedades mecánicas y físicas para operar en las condiciones que el proceso se desarrolle, para el caso de la decoloración, permite remover cuerpos de color, materiales coloidales, materiales orgánicos e inorgánicos del azúcar mediante mecanismos de adsorción e intercambio iónico, para lo cual tenemos resinas de poliestireno y poliacrilamida.
2. El número de columnas de resinas intercambio para esta aplicación en la industrias de bebidas gaseosas depende del color de ingreso y del tipo de azúcar a tratar, es decir si es blanca o rubia. Es importante hacer pruebas piloto para determinar la combinación de resinas de poliestireno y poliacrilamida para llegar al color deseado.
3. El empleo de resinas de intercambio para decoloración de soluciones azucaradas no provoca la inversión de la sacarosa (conversión en glucosa y fructosa) debido a que no existe una disminución del pH en este proceso, sin embargo el empleo de carbón activado para la decoloración provoca este fenómeno que implica mayor consumo de azúcar para obtener una concentración o grado Brix final. Las resinas empleadas para este proceso de decoloración tienen en su composición el anión Cloruro como forma de intercambio;
4. Las resinas de intercambio para decoloración no adsorben sacarosa por lo que no existe una pérdida de la concentración o grado Brix de la solución al pasar por las columnas de intercambio, sin embargo el uso de carbón activado genera una disminución porcentual del grado Brix que involucra mayor consumo de azúcar o sacarosa para mantener una concentración o grado Brix de la solución.

V. RECOMENDACIONES

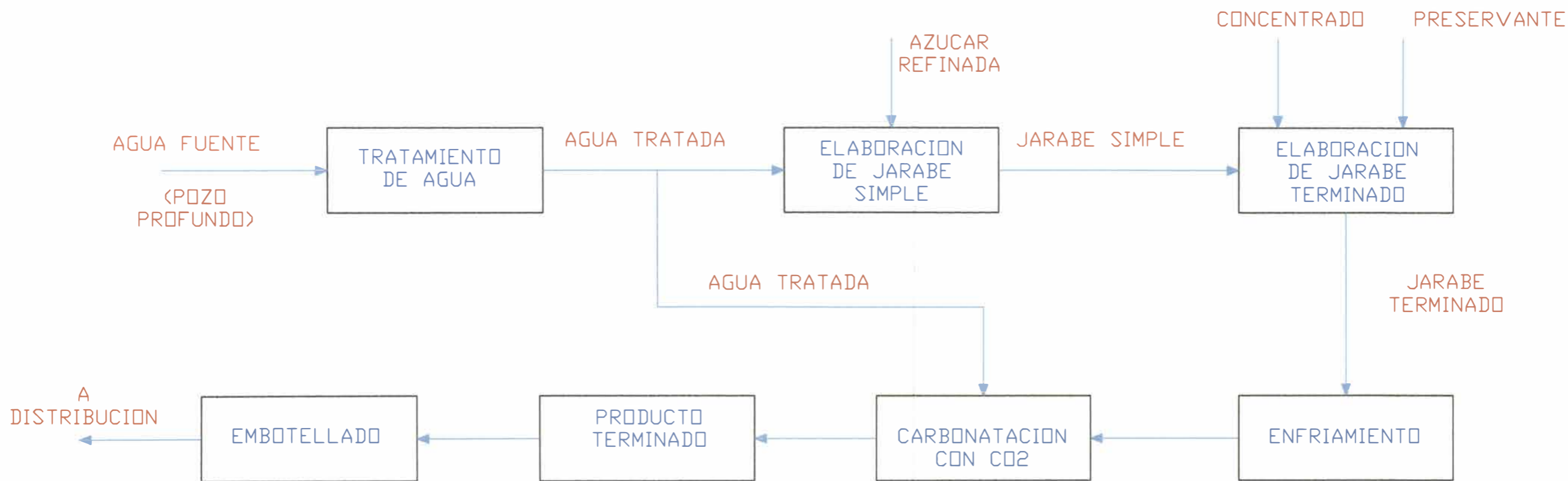
1. Se recomienda usar el arreglo patentado por LEWATIT – Proceso Liftbed que consta que el ingreso del jarabe simple sea por la parte inferior de la columna con el objetivo de aprovechar todo el volumen de resina en el tanque o columna de intercambio.
2. Para un óptimo uso de las resinas, se recomienda cumplir con el valor del color (ICUMSA) en la alimentación del jarabe simple a la columna recomendada por el fabricante de lo contrario podemos incurrir en costos extras de operación.
3. Si el valor de color (ICUMSA) sobrepasa lo sugerido por el fabricante, se sugiere usar otros métodos de decoloración., como por ejemplo: carbón activado.

VI. BIBLIOGRAFIA

1. C.P. Chen, James (1997). MANUAL DEL AZÚCAR DE CAÑA
2. Kart Soest, Hans. LEWATIT ION EXCHANGE RESIN FOR DECOLORISATION OF SUGAR SYRUPS.
3. Bayer AG. "LEWATIT THE BETTER CHANGE"
4. Stevens, Rex R. (1988). "PROCESS FOR DECOLORIZING AQUEOUS SUGAR SOLUTION", Patente N° 4,871, 397.
5. Stevens, Rex R. (1989). PROCESS FOR DECOLORIZING AQUEOUS SUGAR SOLUTION VIA ADSORBENT RESINS AND DESORPTION OF COLOR BODIES FROM THE ADSORBENT RESINS, Patente N° 4,950, 332.

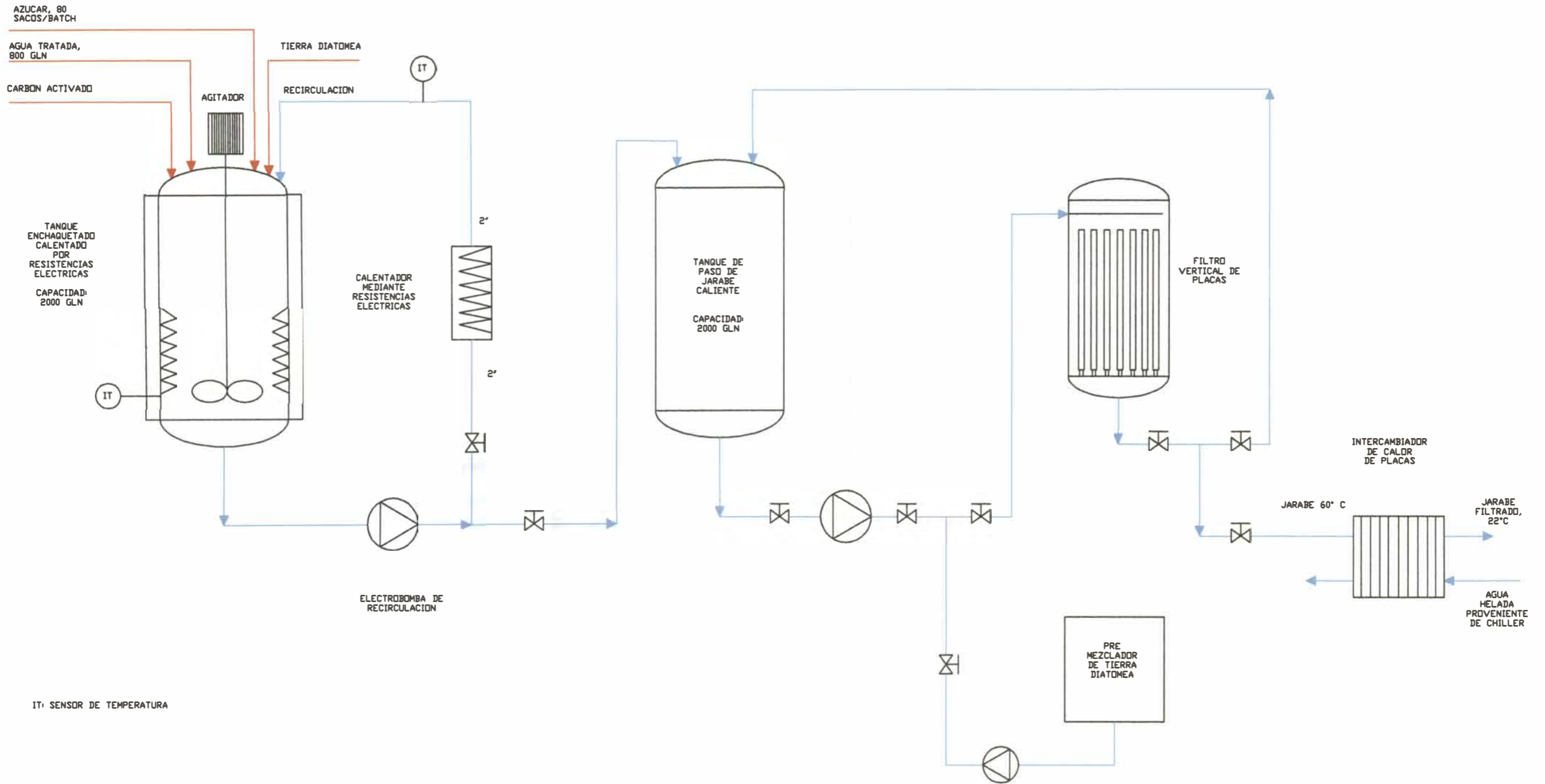
VII. APÉNDICE

**APENDICE I. DIAGRAMA DE FLUJO PARA LA ELABORACION DE
GASEOSAS**



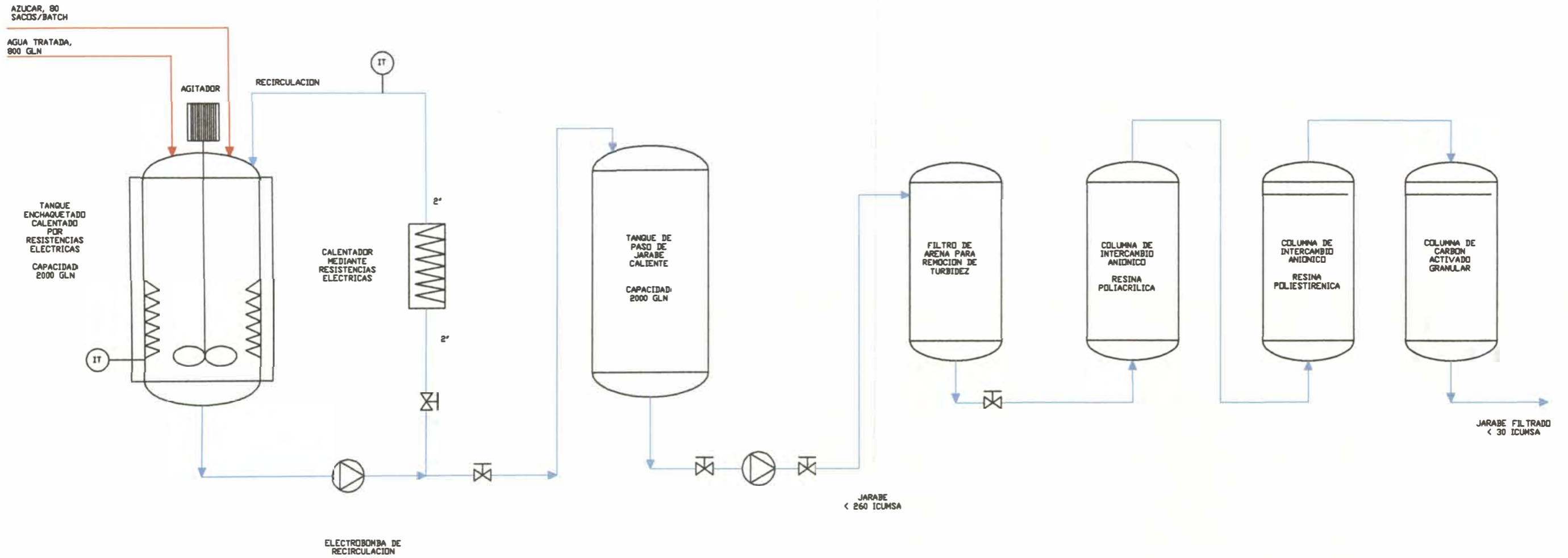
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						EMBOTELLADORA DON JORGE SA		
						NAME / TITULO		
						DIAGRAMA DE FLUJO PARA ELABORACION DE GASEOSAS		
								UNIVERSIDAD NACIONAL DE INGENIERIA-FIQMT
						BY / POR	SCALE / ESCALA	
						C.M.	S/E	
						DATE / FECHA	NUMBER / NUMERO	
0	10.04.10	C.M.	A.R.	A.R.	Para Aprobación	10.04.10	D1	
REV	FECHA	DIBUJ	REVIS	APRO	REVISION			

APENDICE II. FABRICACIÓN DEL JARABE SIMPLE



						CUSTOMER / CLIENTE		
						EMBOTELLADORA DON JORGE SA		
						NAME / TITULO		
						FABRICACION DE JARABE SIMPLE		
							UNIVERSIDAD NACIONAL DE INGENIERIA-FIQMT	
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REV	FECHA	DIBUJ	REVIS	APRO	REVISION	DATE / FECHA 10.04.10		NUMBER / NUMERO D1

**APENDICE III. PROCESO DE DECOLORACION DEL JARABE SIMPLE
CON RESINAS DE INTERCAMBIO IÓNICO**



IT: SENSOR DE TEMPERATURA

						CUSTOMER / CLIENTE		
						EMBOTELLADORA DON JORGE SA		
						NAME / TITULO		
						PROCESO DE DECOLORACION DEL JARABE SIMPLE CON RESINAS DE INTERCAMBIO IONICO		
						UNIVERSIDAD NACIONAL DE INGENIERIA-FIQMT		
0	10.04.10	C.M.	A.R.	A.R.	Para Aprobación	BY / POR C.M.	SCALE / ESCALA S/E	
REV	FECHA	DIBUJ	REVIS	APRO	REVISION	DATE / FECHA 10.04.10	NUMBER / NUMERO D1	

VIII. GLOSARIO

CUERPOS DE COLOR: las sustancias (colorantes provenientes del azúcar) que dan color al jarabe simple.

REACCION DE MAILLARD: La reacción de Maillard (técnicamente: glucosilación o glicación no enzimática de proteínas) se trata de un conjunto complejo de reacciones químicas que se producen entre las proteínas y los azúcares reductores que se dan al calentar (no es necesario que sea a temperaturas muy altas) los alimentos o mezclas similares.

Los azúcares o carbohidratos pueden ser monosacáridos, disacáridos, trisacáridos, oligosacáridos y polisacáridos. Los monosacáridos reaccionan de acuerdo a los grupos hidroxilo y carbonilo que poseen. Los disacáridos y los polisacáridos se pueden hidrolizar para producir monosacáridos.

Los azúcares que dan resultados positivos con las soluciones de Tollens, Benedict ó Fehling se conocen como azúcares reductores, y todos los carbohidratos que contienen un grupo hemiacetal o hemicetal dan pruebas positivas. Los carbohidratos que solo contienen grupos acetal o cetal no dan pruebas positivas con estas soluciones y se llaman azúcares no reductores.

Los azúcares reductores provocan la alteración de las proteínas mediante la reacción de glucosilación no enzimática también denominada reacción de Maillard o glicación.

NTU: La turbidez se mide en Unidad Nefelométrica de turbidez, o Nefelometric Turbidity Unit (NTU), es la unidad de medida para la turbidez.

GRADO BRIX: Los grados Brix (símbolo °Bx) miden el cociente total de sacarosa disuelta en un líquido. Una solución de 25 °Bx tiene 25 g de azúcar (sacarosa) por 100 g de líquido o, dicho de otro modo, hay 25 g de sacarosa y 75 g de agua en los 100 g de la solución. Los grados Brix se miden con un sacarímetro, que mide la gravedad específica de un líquido, o, más fácilmente, con un refractómetro.

FDA. La *FDA* o *Food and Drug Administration* (*Administración de Alimentos y Fármacos*, por sus siglas en inglés) es la agencia del gobierno de los Estados Unidos responsable de la regulación de alimentos (tanto para seres humanos como para animales), suplementos alimenticios, medicamentos (humanos y veterinarios), cosméticos, aparatos médicos (humanos y animales), productos biológicos y productos eméticos.

USP. La United States Pharmacopeia (USP) es una autoridad oficial que da los estándares de la medicina y otros productos de la salud y cuidado de las personas que son manufacturados o vendidos en los Estados Unidos.

ICUMSA. El estándar de la medida de color de la industria azucarera es la Comisión Internacional para la Uniformidad de los Métodos de Análisis del color del Azúcar (en inglés, International Commission for Uniform Methods of Sugar Analysis). El color ICUMSA es el valor del índice de absorbancia multiplicado por 1000. Los valores resultantes se designan como unidades ICUMSA (U.I.)

$$U.I. = a_a \times 1000 = \frac{A_s}{bc} \times 1000$$

SUSTANCIA SECA. Es la materia soluble en un líquido cuya unidad de medida es ° Brix.

IX. ANEXOS

United States Patent [19]

Stringfield et al.

[11] Patent Number: 4,950,332

[45] Date of Patent: Aug. 21, 1990

[54] **PROCESS FOR DECOLORIZING AQUEOUS SUGAR SOLUTIONS VIA ADSORBENT RESINS, AND DESORPTION OF COLOR BODIES FROM THE ADSORBENT RESINS**

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[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **316,058**

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Related U.S. Application Data

[63] Continuation of Ser. No. 169,538, Mar. 17, 1988, abandoned, and a continuation-in-part of Ser. No. 169,537, Mar. 17, 1988, abandoned.

[51] Int. Cl.⁵ **C13D 3/12; C13D 3/14**

[52] U.S. Cl. **127/55; 127/46.2; 127/49; 502/402; 210/670; 210/660; 210/663; 426/271**

[58] Field of Search **127/55, 46.2, 46.1, 127/46.3, 49; 502/402; 210/670, 660, 663; 426/271**

[56] References Cited

U.S. PATENT DOCUMENTS

2,578,938	12/1951	Trenton et al. .
3,122,456	2/1964	Meier et al. .
3,966,489	6/1976	Barrett et al. 127/46.2
4,191,813	3/1980	Reed et al. .
4,193,817	3/1980	Dillman et al. .
4,263,407	4/1981	Reed, Jr., .
4,382,124	5/1983	Meitzner et al. .

FOREIGN PATENT DOCUMENTS

203556	10/1983	German Democratic Rep. .
220964	4/1985	German Democratic Rep. .
2209965	4/1985	German Democratic Rep. .
229992	11/1985	German Democratic Rep. .
249703	9/1986	German Democratic Rep. .
249190	9/1987	German Democratic Rep. .
249193	9/1987	German Democratic Rep. .
249194	9/1987	German Democratic Rep. .
249274	9/1987	German Democratic Rep. .

Primary Examiner—H. M. Sneed

Assistant Examiner—Chung K. Pak

[57] ABSTRACT

A process for decolorizing an aqueous sugar solution by contacting the solution with an adsorbent resin, wherein the adsorbent resin is a macroporous copolymer being post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst and functionalized with hydrophilic groups prior to contact with the aqueous sugar solution.

33 Claims, No Drawings

PROCESS FOR DECOLORIZING AQUEOUS SUGAR SOLUTIONS VIA ADSORBENT RESINS, AND DESORPTION OF COLOR BODIES FROM THE ADSORBENT RESINS

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of copending U.S. application Ser. No. 169,538, filed Mar. 17, 1988, now abandoned, and U.S. application Ser. No. 169,537, filed Mar. 17, 1988, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a process for decolorizing aqueous sugar solutions with an adsorbent resin prepared under suspension polymerization conditions commonly used for ion exchange resins.

Decolorization is a key process in sugar refining. Traditionally, aqueous sugar solutions are decolorized with carbon adsorbents, such as bone char or granular and powdered activated carbon. Unfortunately, the use of carbon has some negative features. In decolorizing with activated carbon, the equipment used in the process is expensive, difficult to operate and to maintain. Another negative feature of carbon is that carbon is abrasive so it is hard on the equipment employed, thereby adding to the replacement cost of the equipment. The fuel for thermal regeneration and carbon replacement of burned carbon are also expensive.

Ion exchange resins have been used to demineralize and decolorize sugar solutions. Unfortunately, the capacity of conventional ion exchange resins for adsorbing color bodies from solution is low relative to the adsorptive capacity of carbon, and the physical stability of some resins used for decolorization is poor. Further, loaded resins require regeneration with strong acids, strong bases, or concentrated salt solutions, which frequently do not remove a substantial quantity of the adsorbed components from the resins, and therefore such resins are prone to fouling during use. These resin characteristics significantly increase the costs associated with using ion exchange resins for decolorizing aqueous sugar solutions, and thus detracts from their commercial viability.

As examples of some of the deficiencies associated with the use of ion exchange resins for decolorizing sugar solutions, the following patents, which describe such processes are discussed and analyzed, U.S. Pat. No. 3,122,456; U.S. Pat. No. 2,578,938; and U.S. Pat. No. 4,193,817.

U.S. Pat. No. 3,122,456 discloses a method of purifying and decolorizing sugar solutions with "spongy" synthetic ion exchange resins. The resins are prepared from crosslinked copolymers permeated by small cavities or veins. Unfortunately, not only do these spongy resins exhibit an adsorptive capacity less than the capacity of carbon, but they also swell considerably upon contact with aqueous solutions - from 200 to 500 percent of their original dry volume. Thus, the resins have very poor physical stability, particularly during acid and base cycling which would be necessary to decolorize a sugar solution and to regenerate the resin. The high swellability and the poor physical stability of the resins additionally increases their tendency to foul during regeneration.

U.S. Pat. No. 2,578,938 discloses a method of decolorizing sucrose solutions with a lightly crosslinked ion

exchange resin. Unfortunately, this resin exhibits the same characteristics associated with the spongy resins, and therefore represents a poor alternative to carbon for decolorizing sugar solutions.

U.S. Pat. No. 4,193,817 discloses decolorizing a bottler's sugar solution with a strong base anion exchange resin. Once again the adsorptive capacity of the resin is poor relative to that of carbon. The resin is regenerated by first contacting the resin with an aqueous solution of sodium chloride and either an alkali metal or alkaline earth metal hydroxide (required to convert resin to hydroxide ion form) and then contacting the resin with an aqueous solution of either sodium chloride or hydrochloric acid (required to convert resin to the desired chloride ion form for subsequent decolorization of sugar solution). Unfortunately, the high dry weight capacity of the resin requires using large amounts of base or acid regenerants, which increase regeneration cost.

In view of the deficiencies of the prior art, a process for decolorizing sugar solutions with an adsorbent having an adsorptive capacity similar to that of carbon is needed. Furthermore, a process employing an effective adsorbent with good physical properties that can be easily and cost-effectively regenerated is needed.

SUMMARY OF THE INVENTION

The present invention is a process for decolorizing an aqueous sugar solution containing color bodies. The process comprises the step of contacting an aqueous sugar solution with an effective amount of an adsorbent resin so as to adsorb color bodies from the aqueous sugar solution onto the adsorbent resin, wherein the adsorbent resin is derived from a macroporous copolymer of a monovinyl aromatic monomer and a crosslinking monomer, where the macroporous copolymer has been post-crosslinked in the swollen state in the presence of a Friedel-Crafts catalyst and functionalized with hydrophilic groups.

The process provides an effective means for decolorizing an aqueous sugar solution without using carbon adsorbents. The adsorbent resin can be as effective as carbon in adsorbing or removing color bodies from sugar solutions. The post-crosslinking of the macroporous copolymer in a swollen state increases the surface area of the copolymer, increases porosity, reduces average pore size, reduces shrink/swell, and imparts rigidity to the copolymer structure.

Moreover, even after functionalizing the copolymer to form the resin, the adsorbent resin maintains the above described properties. In addition, after functionalization, the resin has hydrophilic characteristics. These properties enhance the adsorptive capacity of the resin relative to conventional ion exchange resins used for decolorization. Because of reduced shrink/swell, increased rigidity of the resin structure, and other properties derived from post-crosslinking, the adsorbent resin can be easily regenerated.

DETAILED DESCRIPTION OF THE INVENTION

For purposes of describing this invention, a macroporous copolymer is broadly defined to include copolymers prepared by suspension polymerization of a monomer composition under conditions conventionally used to prepare ion exchange resins, in the presence of one or more progenic diluents using quantities sufficient to

cause phase separation of the prepared copolymer from the diluent. Although, it should be noted that there are many other polymerization techniques known in the art for preparing copolymers which could be useful in polymerization herein.

When a macroporous copolymer is contacted with a swelling solvent, such as chloromethyl methyl ether, its structure is characterized by the presence of regions of densely packed polymer chains separated by pores, often referred to as mesopores (50 to 200 Å and macropores (>200 Å). The nonuniformity of the internal structure of a swollen macroporous copolymer causes the copolymer to appear opaque because of its ability to refract light. If inert diluents or swelling solvents are removed from the macroporous copolymer, for example by subjecting the copolymer to vacuum or steam distillation, then in many instances the pores will collapse from the stress of internal pressures created by increased attractive forces among the regions of packed polymer chains, and the copolymer would then appear transparent or translucent. A class of macroporous copolymers has been developed which retains its porous structure even upon removal of inert diluents or swelling solvents. Such macroporous copolymers are referred to as "macroreticular" copolymers and are described in U.S. Pat. No. 4,382,124. They are characterized by their opaque appearance, regardless of whether or not the copolymer is examined in the presence or absence of inert diluents or swelling solvents.

Processes for preparing macroreticular copolymers of a monovinyl aromatic monomer and a crosslinking monomer, which have been post-crosslinked with a polyfunctional alkylating or acylating compound in a swollen state in the presence of a Friedel-Crafts catalyst, are disclosed in U.S. Pat. Nos. 4,191,813 and 4,263,407, herein incorporated by reference. Such macroreticular copolymers are referred to as "macronet polymeric adsorbents". A macronet polymeric adsorbent can be functionalized with hydrophilic groups using conventional methods for functionalizing copolymers which are prepared via suspension polymerization with ion exchange groups. For example, the polymeric adsorbent can be functionalized by aminating a chloromethylated polymeric adsorbent with either a dimethylamine, trimethylamine, or dimethylethanolamine, depending on whether weak base or strong base functionality is desired. Similarly, the macronet polymeric adsorbent can be functionalized by sulfonation. Alternatively, a chloromethylated polymeric adsorbent can be functionalized by solvolysis at elevated temperatures.

The most preferred process for preparing adsorbent resins which have been post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst is described in East German Pat. No. DD 249,274 A1, herein incorporated by reference. This patent describes post-crosslinking a "solvent-free", chloromethylated macroporous copolymer of styrene and divinylbenzene. After chloromethylation, the copolymer is first contacted with a washing agent, such as methanol, and then the washing agent is removed by either drying the washed copolymer or extracting the washing agent with the swelling solvent used for the subsequent post-crosslinking reaction. After post-crosslinking the chloromethylated copolymer, the copolymer can be functionalized with hydrophilic groups in the conventional manner, thereby producing a useful adsorbent resin. If it is desirable, functionalization could also be performed before post-crosslinking the copolymer.

Although the East German patent only describes a process for preparing adsorbent resins from macroporous copolymers of styrene and divinylbenzene, the process can be used to prepare other macroporous copolymers of a monovinyl aromatic monomer and a crosslinking monomer. These copolymers can be used to produce other adsorbent resins which can be employed to decolorize aqueous sugar solutions.

Regardless of the method used for functionalizing the post-crosslinked macroporous copolymer, after functionalization, the adsorbent resin's hydrophilic character increases its efficiency to adsorb color bodies from sugar solutions and desorption of those color bodies from the resin. Desorption can be accomplished with an aqueous base or an organic solvent, such as ethanol. Preferably, the macroporous copolymer is functionalized by first chloromethylating the copolymer, post-crosslinking the copolymer and then aminating the chloromethylated post-crosslinked copolymer with dimethylamine, trimethylamine or dimethylethanolamine. Most preferably, the post-crosslinked macroporous copolymer is functionalized by aminating the chloromethylated copolymer with dimethylamine. Using conventional ion exchange terminology, an adsorbent resin functionalized in this manner and then contacted with an acidic solution is thus converted to its acid form, which is the form desired for decolorizing many aqueous sugar solutions.

Preferred monovinyl aromatic monomers are styrene and its derivatives, such as α -methylstyrene and vinyl toluene; vinyl naphthalene; vinylbenzyl chloride and vinylbenzyl alcohol. Crosslinking monomers broadly encompass the polyvinylidene compounds listed in U.S. Pat. No. 4,382,124. Preferred crosslinking monomers are divinylbenzene (commercially available divinylbenzene containing less than about 45 weight percent ethylvinylbenzene), trivinylbenzene, and ethylene glycol diacrylate.

The preferred macroporous copolymer is a copolymer of up to about 99.75 weight percent styrene with the balance divinylbenzene. Another preferred macroporous copolymer is a copolymer of about 40 to about 60 weight percent styrene, about 40 to about 60 weight percent vinylbenzyl chloride and about 1 to about 20 weight percent divinylbenzene. The macroporous copolymers may contain minor amounts of other monomers, such as the esters of acrylic and methacrylic acid, and acrylonitrile.

The crosslinker serves to increase the physical stability of the adsorbent resin. The amount of crosslinker required depends significantly on the process conditions used to prepare the copolymer and can range anywhere from about 1 to about 45 percent by weight of total monomer, preferably from about 4 to about 8 percent by weight.

Post-crosslinking in a swollen state displaces and rearranges polymer chains, causing an increase in the number of micropores (<50Å diameter) and mesopores. This increases porosity and surface area and decreases average pore size. Just as significantly, post-crosslinking also imparts rigidity to the polymer, which reduces its tendency to shrink or swell upon contact with an aqueous solution (often referred to in the ion exchange art as the "shrink/swell") and reduces its dry weight capacity when functionalized, which is an indication of its ion exchange capacity. These properties as characterized above increase the capacity of the adsorbent resin to adsorb color bodies, increase its permeabil-

ity to sugar solutions, and increase its physical and dimensional stability.

Furthermore, the reduced shrink/swell and dry weight capacity of the adsorbent resin, which post-crosslinking induces, is conducive to simple, inexpensive and efficient regeneration once color bodies are loaded onto the resin. The reduced dry weight capacity allows desorption of color bodies from the loaded resin with a dilute base. Concentrated bases or acids are unnecessary for regeneration or cleaning. The reduced shrink/swell property allows the resin to maintain sufficient porosity to minimize entrapment of color bodies, and this property in combination with the reduced dry weight capacity reduces the tendency of the resin to retain color bodies during regeneration.

The amount of post-crosslinking required for any given application is an amount effective to achieve the adsorbent resin properties described above to the extent desired.

The adsorbent resin preferably has a surface area of about 150 to about 2100 square meters per gram of dry adsorbent resin (m^2/g), more preferably about 700 to about 1400 m^2/g . Surface area is measured by BET nitrogen adsorption techniques. Porosity ranges from about 0.10 to about 0.70 cubic centimeters of pore volume per cubic centimeter of resin (cc/cc), preferably about 0.43 to about 0.58 cc/cc , as calculated from BET nitrogen adsorption techniques. The porosity contributed by micropores ranges from about 30 to about 100 percent, preferably about 30 to about 50 percent, depending on the resin characteristics. Percent shrink/swell ranges below about 15 percent, more preferably below about 7 percent, and most preferably below about 4 percent. Percent shrink/swell is determined by measuring the volume expansion or contraction of the adsorbent resin when subjected to hydration or a change in ionic form. The dry weight capacity, determined according to conventional methods used for characterizing ion exchange resins, ranges from greater than zero to about 4.0 milliequivalent per gram (meq/g), preferably from greater than zero to about 2.0 meq/g . If the macroporous copolymer is functionalized by solvolysis, for example by contact with water or an alcohol, then the dry weight capacity is essentially zero.

The adsorbent resin can be used in the form of beads, pellets or any other form desirable for decolorizing aqueous sugar solutions. If the adsorbent resin is used in the form of beads, bead size ranges from about 10 to about 1000 microns (μ), preferably from about 100 to about 800 μ , and more preferably from about 300 to about 800 μ .

Examples of aqueous sugar solutions that are advantageously treated according to the present invention include carbohydrate solutions derived from corn starch, such as corn syrup, high fructose corn syrup, dextrose, and sorbitol; sucrose, beet and cane sugar, palm sugar, maple sugar; fruit juices, either natural or processed, such as pear, apple, grape and pineapple mill juices; sugar solutions derived from sorghum; and high fructose syrups derived from tapioca, inulin and potato starch. Preferably, the sugar solution is a solution of corn syrup, high fructose corn syrup, sorbitol, sucrose or dextrose.

The term "decolorizing" refers to removing color bodies from solution to the extent necessary or desired. The decolorization of sugar solutions and more particularly high fructose corn syrup is not an ion exchange phenomena, but is mainly a Van der Waal type interac-

tion of the color bodies with the adsorbent resin. Although identifying color bodies is difficult, it is believed that the color bodies consist of three basic groups. These groups are: (1) caramels, (2) melanoidins and (3) polyphenolics and flavanoids. The caramels are thermal degradation products of sugars; melanoidins are, in general, Maillard reaction products of amine compounds and sugar groups; and the polyphenolics and flavanoids are oxidation products of phenolic compounds derived from a raw sugar solution.

In addition to the three classes of color bodies, there are several noncolored compounds that can develop color, or react to form color bodies during processing or storage of sugar solutions. Such materials are known as color precursors, and for the purpose of describing this invention, the term "color bodies" is intended to include such color precursors. These precursors include amino acids; many hydroxy acids and aldehydes; iron, which complexes with phenolics to make color bodies; 5-hydroxymethyl-2-furfural (HMF); 3-deoxy-d-glucosone (3-D-G) and reducing sugars. These materials often have low molecular weights and are difficult to remove from a sugar solution.

The degree of decolorization necessary or desired will vary from industry to industry or solution to solution. For example, in the beet and cane sugar industry, solutions typically have color levels up to thousands of Reference Base Units (RBU), which is defined more fully hereinafter, with the goal of removing sufficient color bodies so that the solutions have color levels no more than hundreds of RBU. In the high fructose corn syrup industry, color levels rarely go beyond a few hundred RBU with the goal of producing a water white syrup having only a few RBU of color.

The adsorbent resin and the sugar solution may be contacted using conventional methods which result in intimate contact between the resin and the sugar solution. Suitable methods include fluidized beds, stirred tanks, batch tanks, and cocurrent and countercurrent flow columns. The contacting may occur batchwise, semi-batchwise, continuously or semi-continuously. Preferably, the solution is contacted with the resin continuously in a packed column.

The residence time required for contact between the adsorbent resin and the sugar solution depends on the following: (1) the properties of the resin, (2) the amount of color bodies initially present, (3) the level of decolorization desired, (4) the amount of resin used, (5) the viscosity of the sugar solution, (6) the concentration of dissolved sugar (often referred to as dissolved solids), (7) the processing temperature, and (8) the pH of the sugar solution. Therefore, the residence time must be determined empirically. Preferably, the residence time ranges from about 0.1 hours (10 bed volumes/hr) to about 10 hours (0.1 bed volumes/hr), more preferably about 0.12 hours (8 bed volumes/hr) to about 1 hour (1 bed volume/hr), and most preferably about 0.17 hours (6 bed volumes/hr) to about 0.5 hours (2 bed volumes/hr).

The temperature should remain below the temperature at which the sugar solution is adversely affected. Generally, temperatures ranging from about 20° C. to about 80° C. are operable. Preferably, the temperature ranges between about 38° C. and about 55° C.

The amount of adsorbent resin required, largely depends on equipment configuration, concentration of dissolved solids, the level and type of color bodies present, and the level of decolorization desired. Treatment

rates are often expressed in terms of pounds of dry solids that are treated per cubic foot of the adsorbent resin, (lbs. D.S./C.F. resin). Suitable treatment rates range from about 25 to about 10,000 lbs. D.S./C.F. resin: preferably from about 500 to about 5,000 lbs. D.S./C.F. resin; and most preferably from about 1,000 to about 4,000 lbs. D.S./C.F. resin.

The pH of the sugar solution is preferably maintained at a level which allows for the optimum adsorption of color bodies by the adsorbent resin. The pH of the sugar solution prior to decolorization depends on previous processing steps. It is desirable to contact the adsorbent resin with the sugar solution at a pH ranging from about 1 to about 7, preferably from about 3 to about 6, and more preferably from about 4 to about 5.

The amount of dissolved sugar present in the sugar solution will vary with the sugar source. The amount of dissolved sugar ranges up to about 70 weight percent with about 20 to about 50 weight percent being more preferred.

Once color bodies are loaded onto the adsorbent resin, it is desirable and preferable to desorb those color bodies from the resin using a regeneration process that takes advantage of existing equipment and process streams available to the sugar refiner. Additionally, it would be advantageous to avoid the requirement of transferring the resin from a decolorization facility to a regeneration facility. Therefore, in the preferred process, the adsorbent resin is used in a packed column not only to decolorize the sugar solution, but also to regenerate the resin for the next decolorization cycle.

As described above, the reduced dry weight capacity of an adsorbent resin allows desorption of color bodies from the loaded resin with a dilute base. This is particularly advantageous for the sugar refiner because a dilute base is readily available from a waste stream: namely, the regeneration effluent from an anion exchange resin used for demineralizing the aqueous sugar solution.

An aqueous sugar solution is demineralized by removing cationic and anionic impurities, e.g., Ca^{++} , Mg^{++} , HSO_3^- , Cl^- , and SO_4^{--} . Cationic impurities are removed from the solution by contact with a strong acid cation exchange resin in the hydrogen form. Anionic impurities are subsequently removed by contact with a weak base anion exchange resin in the free base form. The cation exchange resin is regenerated by contact with an aqueous solution of hydrochloric acid or sulfuric acid. The anion exchange resin is regenerated by contact with an aqueous solution of sodium hydroxide, soda ash or ammonium hydroxide.

The composition of the regeneration effluent from the anion exchange resin contains not only sodium hydroxide, soda ash, ammonium hydroxide, or mixtures of these, but also impurities removed from the sugar solution, such as chloride salts or sulfate salts. An effluent contains an aqueous solution with a maximum of about 2 weight percent sodium hydroxide, 1.5 weight percent sodium chloride, and 2 weight percent sodium sulfate. Another typical effluent contains about 2 weight percent ammonium hydroxide, 2 weight percent ammonium chloride, and 2 weight percent ammonium sulfate. Preferably, the effluent is an aqueous solution containing sodium hydroxide, sodium chloride and sodium sulfate.

The degree of desorption of color bodies from the loaded adsorbent resin depends on the hydrogen or hydroxide ion concentration of the regeneration effluent and the amount of effluent contacting the adsorbent

resin. The total number of hydroxide ions should exceed the number of active ion exchange sites which the resin possesses. The hydroxide ion concentration of the effluent when contacted with the resin desirably ranges from about 0.01N to about 2.0N, preferably from about 0.05N to about 0.5N.

The degree of desorption increases as the volume of effluent contacting the resin increases. Therefore, it is usually advantageous to dilute the effluent with water until an optimum balance is reached between hydroxide ion content and volume of effluent. An effective amount of effluent is that which is required to achieve the desired degree of desorption. Preferably, a sufficient volume of effluent contacts the resin to desorb at least about 60 percent of color bodies, more preferably at least about 75 percent, and most preferably at least about 85 percent. Percent desorption is based on Reference Basis Units (RBU).

In a preferred embodiment of this invention, a packed column of adsorbent resin used for decolorizing the aqueous sugar solution is treated prior to contact with the regeneration effluent. The resin is treated by contacting the packed column thereof with an effective amount of water to remove residual sugar, and backwashing the packed column to classify and expand the column and to remove particulate contaminants.

In another preferred embodiment, a desorbed adsorbent resin functionalized with weakly basic groups, for example tertiary amine groups from the amination of the chloromethylated copolymer with dimethylamine, is treated with acid to convert the adsorbent resin to the acid form. As discussed previously, the acid form is the preferred form desired for decolorizing many aqueous sugar solutions.

The treatment can be carried out by first contacting the adsorbent resin used in the process of this invention with an effective amount of water to rinse residual hydroxide ions remaining from prior contact with regeneration effluent. The rinsed adsorbent resin may be converted to the acid form by contact with syrup or an acidic solution, such as: (1) an aqueous solution of hydrochloric or sulfuric acid, (2) an acidic sugar solution, for example a sugar solution effluent from a cation exchange resin or (3) regeneration effluent from a cation exchange resin used for demineralizing an aqueous sugar solution. The amount of effluent contacted with the adsorbent resin is desirably that which is necessary to maintain the pH of the aqueous sugar solution below about 6 when contacted with the treated copolymer.

Although what has been described relates only to the use of an adsorbent resin for decolorizing an aqueous sugar solution, the adsorbent resin can be used in combination with other resins, modifiers, stabilizers, and the like, to improve the performance of the adsorbent resin or to enhance its desirability for other applications. For example, the adsorbent resin can be used in combination with conventional cation and anion exchange resins in mixed bed units for polishing aqueous sugar solutions, particularly high fructose corn syrup.

The following examples illustrate, but are not intended to limit the scope of this invention.

EXAMPLE 1

Six samples of adsorbent resin with varying properties are prepared using the procedures described in East German Pat. No. DD 249,274 A1. Each of the six samples is prepared by post-crosslinking a chloromethylated, macroporous copolymer of styrene and divinyl-

benzene. Each sample is then functionalized by aminating the chloromethylated copolymer with dimethylamine. The properties of each of the six samples, designated as Samples 1-6, are reported in Table 1. Two additional samples of adsorbent resin with differing properties are prepared by aminating the chloromethylated macrorecticular adsorbent copolymer substantially described in Example 4 of U.S. Pat. No. 4,263,407. The properties of each sample, designated as Samples 7-8, are also reported in Table 1.

TABLE I

Sample	Dry Weight Capacity (meq/g)	Porosity (cc/cc)	Surface Area (m ² /g)	Average Pore Size (Å)	Percent Shrink/Swell (ionic form)
C-2*	5.08	0.32	150	123	30
1 ¹	3.53	0.47	400	80	11.5
2 ¹	2.91	0.51	626	63	9
3 ¹	1.99	0.52	1065	45	7
4 ¹	1.21	0.56	1374	18	1.2
5	1.18	0.65	—	—	0
6 ²	0.30	0.57	1696	25	1
7 ²	2.03	0.33	609	32	6.1
8 ²	2.53	0.40	624	31	7.2

C-2 is a macroporous styrene-divinylbenzene copolymer chloromethylated and aminated with dimethylamine to prepare a conventional weak base anion exchange resin.

*Not an example of the present invention.

¹Surface area and average pore size measured by a BET sorption analyzer sold commercially by Micromeritics Instrument Corp. as Digisorb 2500.

²Surface area and average pore size measured by a BET sorption analyzer sold commercially by Quantachrome Corp. at Autosorb 6

In separate runs, varying amounts of the adsorbent resin, Samples 1-3 in the free base form are placed in a 3-necked, 250 ml flask equipped with a stirrer, thermometer, and a heating mantle. In each case, the adsorbent resin is added to the reactor after soaking in water and centrifuging to remove residual water. The high fructose corn syrup (HFCS) to be decolorized is added with an initial RBU value of 440 as measured by the ICUMSA Color Method Four, Schneider, F., 1979, Sugar Analysis ICUMSA, Wharf Road, Peterborough, England. The reactor temperature is maintained between 50° to 60° C. for 30 minutes. The reactor is then cooled in an ice bath to 20° C. The decolorized HFCS is filtered to remove all particulates and the RBU color is measured spectrophotometrically and calculated as described below:

RBU =

$$1000 \times \left[\frac{\text{absorbance @ 420 nm} - 2(\text{absorbance @ 720 nm})}{(b)(c)} \right]$$

RBU=Reference Base Unit

nm=nanometer

b=cell length in cm

c=syrup concentration in gm/ml

Similar runs are performed using Calgon CPG 12/40 mesh granular activated carbon (C-1), a functionalized macroporous copolymer which has not been post-cross-linked (C-2), and Dowex® 66 for comparison purposes.

The results are illustrated in Table II.

TABLE II

Sample	Reference Base Units (RBU) Weight Percent ¹ of Decolorizing Agent in HFCS		
	1 percent	2.5 percent	5 percent
	C-1*	400	—
C-2*	—	243	313
C-3*	478	—	211
1	—	155	140
2	381	—	71
3	—	165	50

C-1 is Type CPG Granular Carbon sold commercially by Calgon Corporation.

C-2 is a macroporous styrene-divinylbenzene copolymer chloromethylated and aminated with dimethylamine to prepare a conventional weak base anion exchange resin.

C-3 is Dowex® 66 macroporous anion exchange resin available from The Dow Chemical Company.

*Not an example of the present invention

¹Weight percent is calculated based on the dry weight of the decolorizing agent.

EXAMPLE 2

The adsorbent resins of Samples 1, 2, and 4-8 are subjected to an equilibrium adsorption test. The procedure of Example 1 is essentially repeated, except that the adsorbent resins are in the hydrochloric acid form rather than the free base form and the untreated HFCS exhibits an RBU value of 353 instead of 440.

The adsorbent resins are placed in the hydrochloric acid form by slurrying the adsorbent resin in the free base form in a solution of 1N hydrochloric acid. After standing for about 1 hour, the adsorbent resin is back-washed with deionized water until the effluent is neutral (pH about 7). The adsorbent resins are then centrifuged to remove excess water.

The results are illustrated in Table III.

TABLE III

Sample	Reference Base Units (RBU) Weight Percent ¹ of Decolorizing Agent of HFCS				
	1 percent	2.5 percent	5 percent	10 percent	20 percent
	C-1*	212	170	119	57
C-2*	200	82	59	58	56
1	100	65	57	45	33
2	98	53	45	29	11
4	107	41	19	7	—
5	100	73	48	24	4
6	185	76	38	30	7
7	150	110	88	57	26
8	173	133	92	61	38

C-1 is Type CPG granular carbon sold commercially by Calgon Corporation.

C-2 is a macroporous styrene-divinylbenzene copolymer chloromethylated and aminated with dimethylamine to prepare a conventional weak base anion exchange resin.

*Not an example of the present invention.

¹Weight percent is calculated based on the dry weight of the decolorizing agent.

Once again, the reduced RBU values illustrated in Table III indicate that the claimed process provides a superior method of decolorizing HFCS.

EXAMPLE 3

In a one-inch column, a dextrose solution containing 30 percent dissolved solids and exhibiting an RBU color value of 40 is contacted with the adsorbent resin designated as Sample 3 of Example 1. The solution is contacted with a 400 ml bed of the adsorbent resin in the HCl form. The flow rate is maintained at 4 bed volumes/hour for a period of time equivalent to 140 bed volumes. The temperature of the dextrose solution is about 50° C.

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The solution exiting the column is analyzed for RBU value and exhibits values from 2 to 6 with an average of 4 RBU through 140 bed volumes. The results illustrate the effectiveness of the present invention as a means of removing color bodies from solutions containing sugar. 5

EXAMPLE 4

In a one-inch column, a dextrose solution containing 50 percent dissolved solids and exhibiting an RBU color value of 390 is contacted with the adsorbent resin designated as Sample 3 of Example 1. The solution is contacted with a 400 ml bed of the adsorbent resin in the HCl form. The flow rate is maintained at 4 bed volumes/hour for a period of time equivalent to 100 bed volumes. The temperature of the dextrose solution is about 50° C. 10 15

After 100 bed volumes, the solution exiting the column is analyzed for RBU value. The RBU value is less than 100. This result illustrates that even at higher RBU values the present invention is effective in removing a major percentage of the color bodies. 20

EXAMPLE 5

In an 8 mm I.D. by 100 mm glass column is loaded 5 ml of adsorbent resin in the hydroxide form having properties similar to the macroporous copolymer designated as Sample 3 of Example 1, except that the post-crosslinked chloromethylated copolymer is aminated with trimethylamine instead of dimethylamine. The column temperature is maintained at 50° C. A beet sugar solution is metered through the column at a rate of 0.2 ml/min. The adsorbance of effluent is continually monitored at a wavelength of 420 nm using a spectrophotometer equipped with a flow cell. The percent color leakage is determined by adjusting the maximum transmission (zero percent color leakage) using deionized water for the lower limit and adjusting the minimum transmission (100 percent color leakage) using the neat beet sugar solution for the upper limit. The percent color leakage is defined as the color not adsorbed by the adsorbent resin. The results are summarized in Table IV under Sample 9. 25 30 35 40 45

TABLE IV

Sample	1 Hr.	Percent Color Leakage				
		2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
C-4*	8.7	16.0	19.8	25.0	29.2	—
9	2.5	4.8	7.5	12.4	17.7	21.5

C-4 is DOWEX® MSA-1 macroporous anion exchange resin available from The Dow Chemical Company. 50

*Not an example of the invention.

The data illustrates the effectiveness of the present invention in removing color bodies from beet sugar solutions compared to a conventional macroporous anion exchange resin. 55

EXAMPLE 6

In a 13 mm diameter column, an apple juice containing 15 percent dissolved solids and exhibiting an RBU color value of 4500 is contacted with the adsorbent resin designated as Sample 3 of Example 1. The juice is contacted with a 10 ml bed of the adsorbent resin in the HCl form. The flow rate is maintained at 6 bed volumes/hour for a period of time equivalent to 30 bed volumes. The temperature of the apple juice is ambient or approximately 20° C. 60 65

The apple juice exiting the column is analyzed for RBU value and exhibits values from 91 to 1035. Within

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the industry, an acceptable RBU color level is 1195. The results illustrate that even at very high RBU values the present invention is effective in removing a major percentage of the color bodies.

EXAMPLE 7

5 ml of the adsorbent resin, essentially the same as Sample 3 of Example 1, in the hydrochloric acid form, is placed in an 8 mm ID × 100 mm glass column. The column temperature is maintained at 50° C. The resin is loaded with color bodies by passing a synthetic dextrose syrup through the resin. The synthetic dextrose syrup contains 50 percent dissolved dextrose, 1.170 mg/liter of NaCl, 150 mg/liter of nitrogen (as glycine), 16.7 mg/liter of 5-hydroxymethyl-2-furfural, 100 ppb of acetaldehyde. Color is imparted to the syrup by heating the solution to 70° C. and adjusting the pH to 8, then cooling the solution to 40° C. and lowering the pH to about 4.0. The syrup has a pH of about 4.0 and exhibits an RBU value ranging from 300-650. The synthetic dextrose syrup is pumped through the column of adsorbent resin at 4 bed volumes per hour until the desired level of decolorization is obtained. The column is then cooled to ambient temperature for the desorption cycle. The resin is washed with water to remove residual sugar.

An aqueous solution of 2.0 percent NaOH, 1.0 percent NaCl, and 0.5 percent Na₂SO₄ is prepared. This caustic solution is representative of a regeneration effluent from an anion exchange resin used for demineralizing an aqueous sugar solution. Three bed volumes of the above solution are diluted in a ratio of 4 parts water to 1 part solution to give a total volume of 15 bed volumes. The loaded adsorbent resin is desorbed by initially contacting the resin with about 5 bed volumes of the diluted caustic solution to substantially convert the adsorbent resin to the free base form and then contacting the adsorbent resin with about 10 bed volumes of the diluted caustic solution at a flow rate of about 1.2 bed volumes per hour to desorb the color bodies.

The percentage of color bodies desorbed from the adsorbent resin is determined by dividing the total amount of color bodies in the caustic regenerant solution by the total amount of color bodies adsorbed from the sugar solution. The results are illustrated in Table V.

TABLE V

Bed Volumes Regenerant	Percent Color Bodies Desorbed
0.3	1.0
1.2	41.2
2.4	88.2
3.6	91.2
6.0	93.4
9.6	96.5

What is claimed is:

1. A process for decolorizing an aqueous sugar solution containing color bodies, comprising the step of contacting an aqueous sugar solution with an effective amount of an adsorbent resin so as to adsorb color bodies from said aqueous sugar solution onto said adsorbent resin, wherein said adsorbent resin is made from a macroporous copolymer of a monovinyl aromatic monomer and a crosslinking monomer, where the macroporous copolymer has been post-crosslinked in the swollen

state in the presence of a Friedel-Crafts catalyst and functionalized with hydrophilic groups.

2. The process of claim 1 wherein the crosslinking monomer is a polyvinylidene monomer.

3. The process of claim 2 wherein the polyvinylidene monomer is divinylbenzene, trivinylbenzene or ethylene glycol diacrylate.

4. The process of claim 3 wherein the monovinyl aromatic monomer is styrene vinylbenzyl chloride, vinylbenzyl alcohol, or vinyl naphthalene.

5. The process of claim 4 wherein the macroporous copolymer contains up to about 99.75 weight percent styrene with the balance divinylbenzene.

6. The process of claim 1 wherein the macroporous copolymer contains from about 1 to about 45 weight percent of the crosslinking monomer.

7. The process of claim 6 wherein the adsorbent resin contains from about 4 to about 8 weight percent of the crosslinking monomer.

8. The process of claim 1 wherein the macroporous copolymer is chloromethylated.

9. The process of claim 1 wherein the macroporous copolymer is post-crosslinked with a polyfunctional alkylating or acylating compound.

10. The process of claim 1 wherein the post-crosslinked macroporous copolymer is functionalized with dimethylamine, trimethylamine or dimethylethanolamine.

11. The process of claim 1 wherein the post-crosslinked copolymer is functionalized by solvolysis.

12. The process of claim 1 wherein the post-crosslinked copolymer is functionalized by sulfonation.

13. The process of claim 1 wherein the adsorbent resin has a surface area of about 150 to about 2100 m²/g.

14. The process of claim 13 wherein the adsorbent resin has a surface area of about 700 to about 1400 m²/g.

15. The process of claim 1 wherein the adsorbent resin has a porosity of about 0.10 to about 0.70 cc/cc.

16. The process of claim 15 wherein the adsorbent resin has a porosity of about 0.43 to about 0.58 cc/cc.

17. The process of claim 1 wherein the adsorbent resin exhibits a percent shrink/swell below about 7 percent.

18. The process of claim 17 wherein the adsorbent resin exhibits a percent shrink/swell below about 4 percent.

19. The process of claim 1 wherein the dry weight capacity of the adsorbent resin ranges from about greater than zero to about 4.0 meq/g.

20. The process of claim 19 wherein the dry weight capacity of the adsorbent resin ranges from about greater than zero to about 2.0 meq/g.

21. The process of claim 1 wherein the aqueous sugar solution is a solution of corn syrup, a fruit juice, sucrose, or dextrose.

22. The process of claim 1 wherein the aqueous sugar solution is contacted with the adsorbent resin continuously in a packed column.

23. The process of claim 1 wherein the amount of the adsorbent resin employed is from about 1,000 to about 4,000 lbs.D.S./C.F. resin.

24. The process of claim 1 further comprising the step of desorbing color bodies from the adsorbent resin by contacting the resin with a regeneration effluent from an anion exchange resin used for demineralizing the aqueous sugar solution.

25. The process of claim 24 wherein the regeneration effluent is an aqueous solution comprising sodium hydroxide, sodium chloride and sodium sulfate.

26. The process of claim 24 wherein the hydroxide ion concentration of the regeneration effluent ranges from about 0.05N to about 0.5N.

27. The process of claim 24 wherein a sufficient volume of regeneration effluent contacts the adsorbent resin to desorb at least about 85 percent of the color bodies from the copolymer.

28. The process of claim 24 wherein a packed column of the adsorbent resin used for decolorizing the aqueous sugar solution is treated prior to contact with the regeneration effluent by contacting the packed column with an effective amount of water to remove residual sugar and then backwashing the packed column to classify and expand the column and to remove particulate contaminants.

29. The process of claim 24 further comprising the step of contacting the desorbed adsorbent resin with an effective amount of water to remove residual hydroxide ions remaining from contact with the regeneration effluent.

30. The process of claim 29 wherein the post-crosslinked macroporous copolymer is functionalized with dimethylamine, trimethylamine or dimethylethanolamine.

31. The process of claim 30 further comprising the step of converting the adsorbent resin to the acid form by contacting the adsorbent resin with an acidic solution.

32. The process of claim 1 wherein the adsorbent resin is used in combination in a mixed bed unit with a cation exchange and an anion exchange resin.

33. The process of claim 21 wherein the corn syrup solution is high fructose corn syrup.

* * * * *

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,950,332

Page 1 of 4

DATED : August 21, 1990

INVENTOR(S) : Richard T. Stringfield; H. Robert Goltz; Seth I. Norman;
Upen J. Bharwada; Robert L. LaBrie

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page, column 2, in the section [56] FOREIGN PATENT DOCUMENTS, "2209965" should correctly appear --220965--;

Column 1, line 23, after the word "features" insert --.--;

Column 3, line 10, "(50 to 200 Å" should correctly appear --(50 to 200 Å)--;

Column 4, line 31, "toluene:" should correctly appear --toluene;--;

Column 5, line 40, "4 0" should correctly appear --4.0--;

Column 5, line 56, "sorbitol:" should correctly appear --sorbitol;--;

Column 5, line 57, "maple sugar:" should correctly appear --maple sugar;--;

Column 5, line 59, "juices:" should correctly appear --juices;--;

Column 5, line 59, "sorghum:" should correctly appear --sorghum;--;

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,950,332

Page 2 of 4

DATED : August 21, 1990

INVENTOR(S) : Richard T. Stringfield; H. Robert Goltz; Seth I. Norman;
Upen J. Bharwada; Robert L. LaBrie

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 6, line 6, "sugars:" should correctly appear --sugars;--;

Column 6, line 8, "groups:" should correctly appear --groups;--;

Column 6, line 18, "acids:" should correctly appear --acids;--;

Column 6, line 18, "aldehydes:" should correctly appear --aldehydes;--;

Column 6, line 19, "bodies:" should correctly appear --bodies;--;

Column 7, line 5, "resin:" should correctly appear --resin;--;

Column 7, line 6, "resin:" should correctly appear --resin;--;

Column 7, line 36, "stream:" should correctly appear --stream;--;

Column 10, line 19, after TABLE II footnotes and before EXAMPLE 2, insert the following paragraph: --

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,950,332

Page 3 of 4

DATED : August 21, 1990

INVENTOR(S) : Richard T. Stringfield; H. Robert Goltz; Seth I. Norman;
Upen J. Bharwada; Robert L. LaBrie

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

The reduced RBU values illustrated in Table II for Samples 1-3 indicate that the claimed process provides a superior method of decolorizing HFCS.--;

Column 12, line 40, after the word "hour" insert --,--;

Column 12, line 58, after TABLE V insert the following paragraph: --The data illustrates the effectiveness of the synthetic waste regenerant stream in desorbing color bodies from the adsorbent resin.--;

Column 13, line 6, "id" should correctly appear --is--;

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,950,332

Page 4 of 4

DATED : August 21, 1990

INVENTOR(S) : Richard T. Stringfield; H. Robert Goltz; Seth I. Norman;

Upen J. Bharwada; Robert L. LaBrie
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 14, line 4, "sucrose," should correctly appear --sucrose--.

**Signed and Sealed this
Third Day of March, 1992**

Attest:

HARRY F. MANBECK, JR.

Attesting Officer

Commissioner of Patents and Trademarks

United States Patent [19]

Stevens

[11] Patent Number: 4,871,397

[45] Date of Patent: Oct. 3, 1989

[54] PROCESS FOR DECOLORIZING AQUEOUS SUGAR SOLUTION

[75] Inventor: Rex R. Stevens, Midland, Mich.

[73] Assignee: The Dow Chemical Company, Midland, Mich.

[21] Appl. No.: 192,749

[22] Filed: May 9, 1988

[51] Int. Cl.⁴ C13D 3/14; C13D 3/12

[52] U.S. Cl. 127/55; 127/46.2; 127/46.3; 502/402

[58] Field of Search 127/55, 46.2, 46.1, 127/46.3, 49; 502/402

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,631,999 3/1953 McMaster et al. 260/88.1
2,785,998 3/1957 Harding et al. 127/46.2
3,417,066 12/1968 Corte et al. 260/88.1
3,637,535 1/1972 Corte et al. 260/2.1
3,966,489 6/1976 Barrett et al. 127/46 A

4,191,814 3/1980 Amick 521/32
4,273,878 6/1981 Amick 521/32
4,427,793 1/1984 Reed et al. 521/32

OTHER PUBLICATIONS

Vysokomolekulyarnye Soedineniya, vol. (a) XXIII, Nr. 8, 1981, pp. 1852-1856, "Features of Porous Structure of Macroporous Low-Basic Anionites Based on Ethylenediamine" by Brutskus, et al.

Primary Examiner—H. M. S. Sneed

Assistant Examiner—Chung K. Pak

[57] **ABSTRACT**

Improved process for decolorizing aqueous sugar solutions by contacting solution with an adsorbent anion exchange resin prepared by aminating a macroporous, chloromethylated copolymer with a polyamine under conditions sufficient to promote crosslinking of unreacted amine sites with chloromethyl groups on the copolymer.

20 Claims, 3 Drawing Sheets

COLOR BODY REMOVAL FROM HIGH FRUCTOSE CORN SYRUP BY EDA FUNCTIONALIZED RESIN (METHYLAL SWELLED)

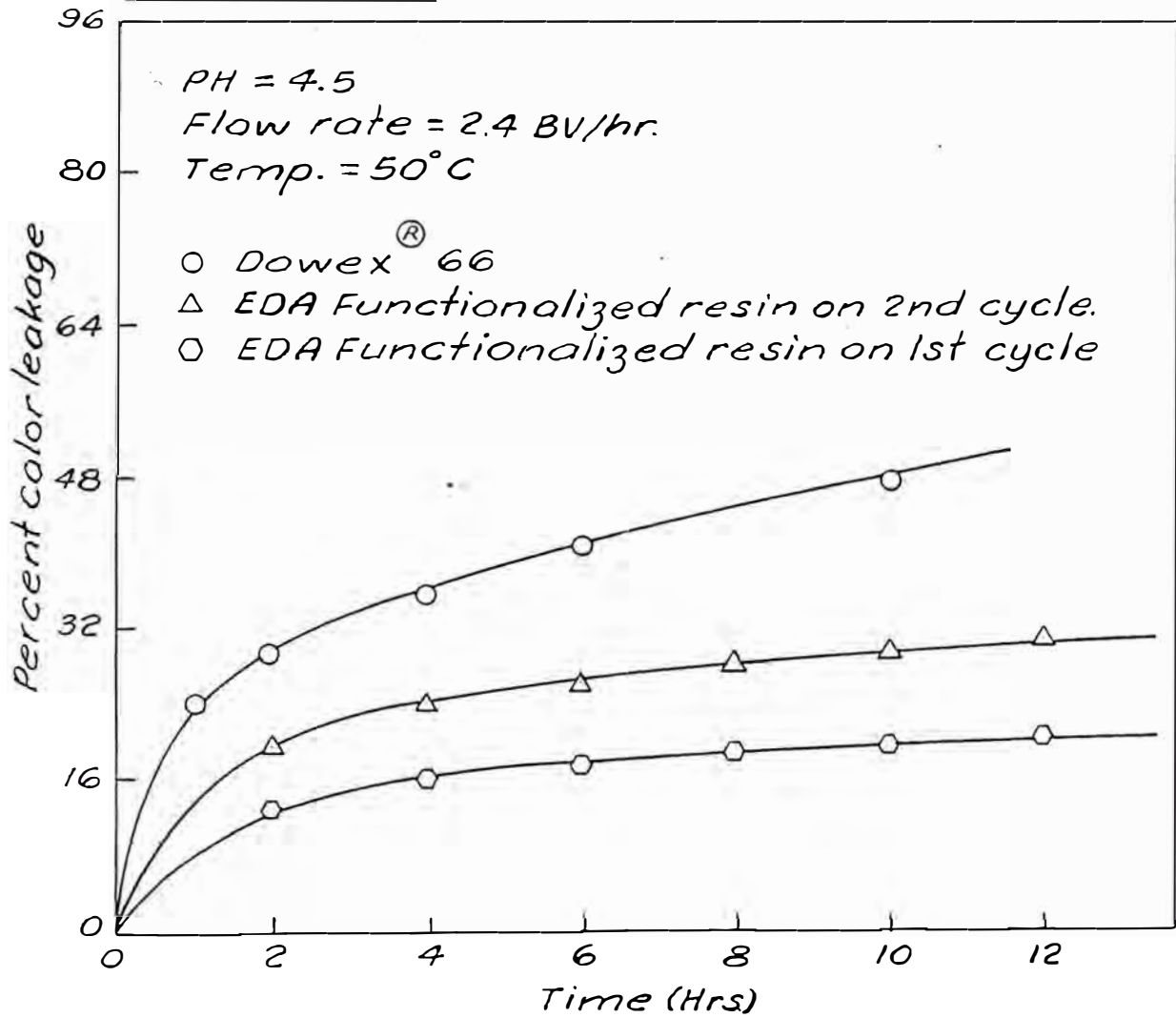


Fig. 1

COLOR BODY REMOVAL FROM HIGH FRUCTOSE CORN SYRUP BY EDA FUNCTIONALIZED RESIN (EDA SWELLED)

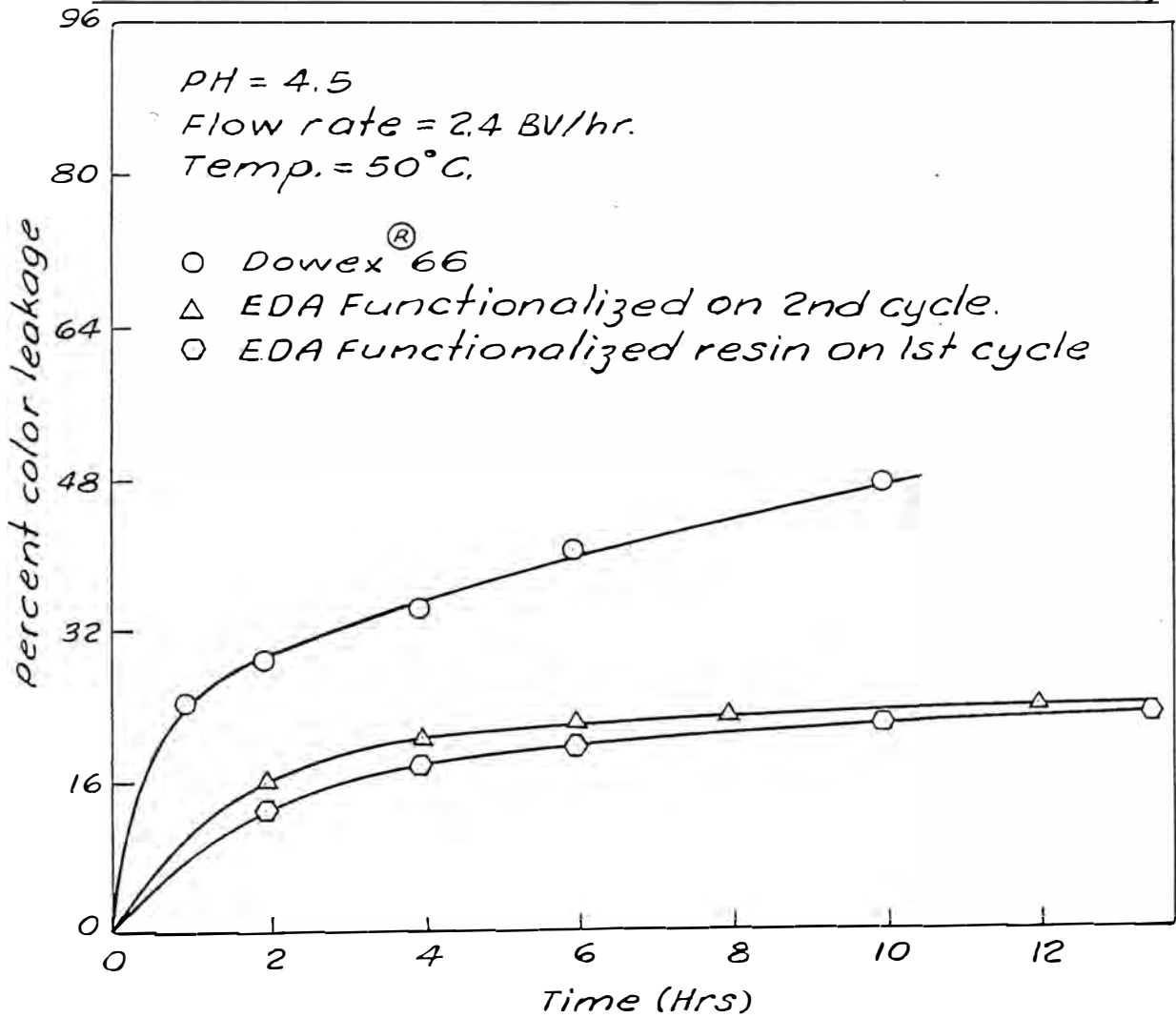


Fig. 2

COLOR BODY REMOVAL FROM ACIDIFIED BEET SYRUP BY DETA FUNCTIONALIZED RESIN (EDC SWELLED)

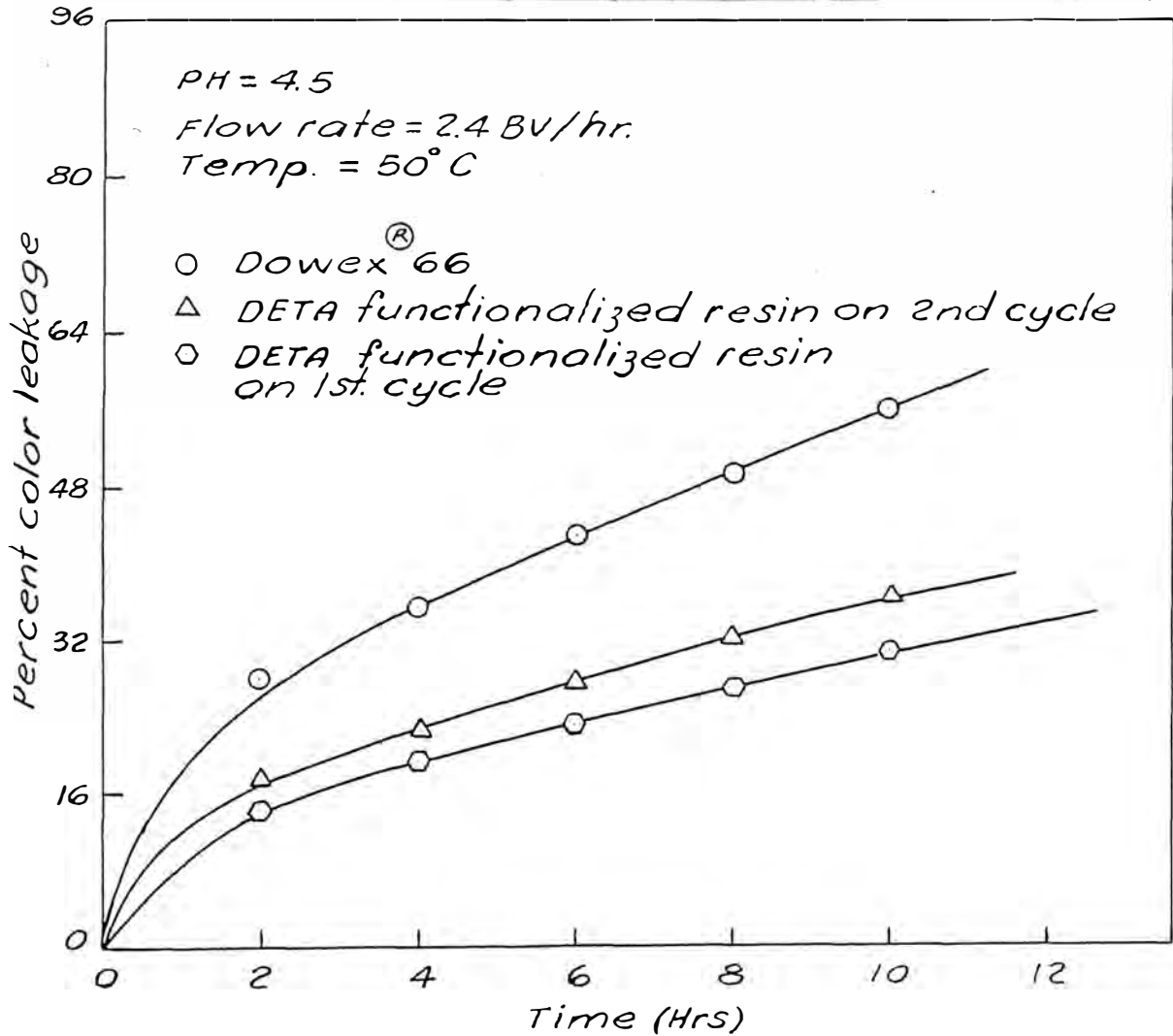


Fig. 3

PROCESS FOR DECOLORIZING AQUEOUS SUGAR SOLUTION

BACKGROUND OF THE INVENTION

The present invention relates to a process for decolorizing aqueous sugar solutions.

Decolorization is a key process in sugar refining. Traditionally, aqueous sugar solutions are decolorized with carbon adsorbents such as bone char or granular and powdered carbon. Unfortunately, carbon adsorbents typically require thermal regeneration to remove adsorbed components from the carbon. Therefore, the cost of regenerating carbon adsorbents increases as fuel costs increase. Further, the thermal regeneration of carbon adsorbents is difficult, time-consuming, and may also destroy an appreciable portion of the carbon.

Ion exchange resins have been used to demineralize and decolorize sugar solutions in an attempt to eliminate the difficulties encountered using carbon as a decolorizer. For example, U.S. Pat. No. 4,193,817 discloses decolorizing a bottler's sugar solution with a strong base anion exchange resin. Unfortunately, the capacity of these resins for adsorbing color bodies is low relative to the adsorptive capacity of carbon. Therefore, a more efficient process for decolorizing aqueous sugar solutions using an ion exchange resin is needed.

SUMMARY OF THE INVENTION

The invention is an improvement in the process of decolorizing an aqueous sugar solution by contacting the solution with an anion exchange resin. The improvement comprises using an adsorbent anion exchange resin prepared by aminating a macroporous, chloromethylated copolymer with a polyamine under conditions sufficient to promote crosslinking of unreacted amine sites with chloromethyl groups on the copolymer.

The improved process of this invention provides an efficient means for decolorizing an aqueous sugar solution. The crosslinking of unreacted amine sites with chloromethyl groups on the copolymer creates an amine-bridged resin that has increased porosity. The increase in porosity enhances the capacity of the resin to adsorb color bodies. Therefore, the polyamine-functionalized resin can decolorize an aqueous sugar solution more efficiently than a conventional anion exchange resin.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-3 are plots of the capacity of polyamine-functionalized resins and a conventional anion exchange resin to decolorize aqueous sugar solutions over time.

DETAILED DESCRIPTION OF THE INVENTION

The polyamine used for amination can be any polyamine that has at least two amine groups, preferably terminal amine groups, each one of which is capable of reacting with a chloromethyl group on the copolymer. Examples of polyamines useful in the process of this invention include, but are not limited to, lower molecular weight aliphatic polyamines such as ethylene diamine, propylene diamine (1,3-diaminopropane), butylene diamine (1,4-diaminobutane), diethylene triamine, and dipropylene triamine; and aromatic diamines such as phenylenediamine and benzidine. The preferred

polyamines are ethylene diamine and propylene diamine.

The preferred copolymer is a crosslinked aromatic copolymer of a polyunsaturated monomer and a monoethylenically unsaturated monomer. Advantageously, at least 50 weight percent of the comonomer composition comprises an aromatic monomer. Preferred polyunsaturated monomers include divinylbenzene (commercially available divinylbenzene containing less than about 45 weight percent ethylvinylbenzene), trivinylbenzene, and ethylene glycol diacrylate. Preferred monoethylenically unsaturated monomers include styrene, α -methylstyrene, vinylpyridine, vinyl toluene, vinyl naphthalene, vinylbenzyl chloride and methyl methacrylate.

The preferred aromatic copolymer is a copolymer of up to about 99.75 weight percent styrene with the balance divinylbenzene. Another preferred copolymer is a copolymer of about 40 to about 60 weight percent styrene, about 40 to about 60 weight percent vinylbenzyl chloride and about 1 to about 20 weight percent divinylbenzene. The copolymers may contain minor amounts of other monomers, such as about 1 to about 4 weight percent acrylonitrile.

The polyunsaturated monomer acts as a crosslinker to increase the physical stability of the copolymer. For the preparation of a macroporous copolymer about 0.25 to about 20 weight percent, preferably about 1 to about 15 weight percent, and more preferably about 4 to about 10 weight percent polyunsaturated monomer is desirable to achieve effective crosslinking.

Exemplary processes for preparing macroporous, chloromethylated copolymers are well known in the art and are sufficiently described in U.S. Pat. Nos. 4,382,124; 4,221,871 and 3,637,535.

In a preferred embodiment, the macroporous, chloromethylated copolymer is expanded in a swelling solvent before amination. Conventional swelling solvents include methylal, dimethoxyethane and dioxane, although any inert solvent capable of swelling the copolymer beads would be adequate. The amount of swelling solvent required is an amount sufficient to swell and slurry the copolymer, and can be readily determined empirically.

The swollen, chloromethylated copolymer is advantageously aminated in the presence of a polar solvent. The polar solvent solubilizes amine hydrochloride salts that form during amination, therefore preventing agglomeration of copolymer particles. The polar solvent also promotes crosslinking of unreacted amine sites with chloromethyl groups on the copolymer. Although any polar solvent is adequate, the preferred polar solvents are water, methanol and ethanol. The amount of polar solvent required can be determined empirically. For water, about 5 to 10 weight percent based on the weight of total solvent is preferred. For methanol, about 10 to 20 weight percent is preferred.

The polar solvent can be mixed with the slurry of copolymer particles before amination, or a mixture of the polar solvent and the polyamine can be prepared. Preferably, the polar solvent is added to the slurry of copolymer particles before amination.

The amount of polyamine generally required for amination can range from about 0.5 to 2 moles of amine per mole of chloromethyl group, preferably from about 0.5 to 1 mole of amine per mole of chloromethyl group. The polyamine is advantageously added to the slurry of copolymer particles continuously at a rate sufficient to

control the temperature of the exothermic amination reaction. Preferably, the temperature is maintained below the boiling point of the solvent system used. When the polyamine is added in this manner, a major portion of the amination reaction occurs in the presence of excess chloromethyl groups. This excess of chloromethyl groups promotes crosslinking of the unreacted amine sites.

After all of the polyamine is added, the amination is completed by raising the temperature to reflux and maintaining reflux for about 1 to 2 hours.

Examples of aqueous sugar solutions that are advantageously treated according to the present invention include carbohydrate solutions derived from corn starch, such as corn syrup, high fructose corn syrup, dextrose, sorbitol, beet and cane sugar, palm sugar, maple sugar; fruit juices, either natural or processed, such as pear, apple, grape and pineapple mill juices; sugar solutions derived from sorghum; and high fructose syrups derived from tapioca, inulin and potatoes. Preferably, the sugar solution is a solution of corn syrup, high fructose corn syrup or dextrose.

The term "decolorizing" refers to removing color bodies from solution to the extent necessary or desired. The decolorization of sugar solutions and more particularly high fructose corn syrup is not an ion exchange phenomena but is mainly a Van der Waal-type interaction of the color bodies with the ion exchange resin. The term "color bodies" refers not only to materials affecting the color of the sugar solution, but also to precursors of such materials. Although identifying color bodies is difficult, it is believed that the color bodies consist of three basic groups. These groups are: (1) caramels, (2) melanoidins and (3) polyphenolics and flavanoids. The caramels are thermal degradation products of sugars; melanoidins are, in general, Maillard reaction products of amine compounds and sugar groups; and the polyphenolics and flavanoids are oxidation products of phenolic compounds derived from a raw sugar solution.

In addition to the three classes of color bodies, there are several noncolored compounds that can develop color, or react to form color bodies during processing or storage of sugar solutions. Such materials are known as color precursors. These precursors include amino acids; many hydroxy acids and aldehydes; iron, which complexes with phenolics to make color bodies; 5-hydroxymethylfurfural (HMF); 3-deoxy-d-glucosone (3-D-G) and reducing sugars. These materials often have low molecular weight and are difficult to remove from a sugar solution.

The degree of decolorization necessary or desired will vary from industry to industry or solution to solution. For example, in the beet and cane sugar industry, solutions typically have color levels up to thousands of Reference Base Units (RBU) with the goal of removing sufficient color bodies so that the solutions have color levels no more than hundreds of RBU. In the high fructose corn syrup industry, color levels rarely go beyond a few hundred RBU with the goal of producing a water white syrup having only a few RBU of color.

The adsorbent anion exchange resin and the sugar solution may be contacted using conventional methods which result in intimate contact between the agent and the sugar solution. Suitable methods include fluidized beds, stirred tanks, batch tanks, and cocurrent and countercurrent flow columns. The contacting may occur batchwise, semi-batchwise, semi-continuously or con-

tinuously. Preferably, the solution is contacted with the agent continuously in a packed column.

The residence time required for contact between the resin and the sugar solution depends on the properties of the agent, amount of color bodies present initially, level of decolorization desired, amount of agent used, viscosity, concentration of dissolved sugar, temperature, and pH. Preferably, the residence time ranges from about 0.1 hours (10 bed volumes/hr) to about 10 hours (0.1 bed volumes/hr), more preferably about 0.12 hours (8 bed volumes/hr) to about 1 hour (1 bed volume/hr), and most preferably about 0.17 hours (6 bed volumes/hr) to about 0.5 hours (2 bed volumes/hr).

The temperature should remain below the temperature at which the sugar solution is adversely affected. Generally, temperatures ranging from about 20° C. to about 80° C. are operable. Preferably, the temperature ranges between about 38° C. and about 55° C.

The amount of anion exchange resin required largely depends on equipment configuration, concentration of dissolved solids, the level and type of color bodies present, and the level of decolorization desired. Suitable amounts of resin range from about 1 to about 0.005 kilograms of resin per kilogram of aqueous sugar solution (kg/kg), preferably about 0.3 to about 0.007 kg/kg, more preferably about 0.017 to about 0.008 kg/kg.

The pH of the sugar solution is preferably maintained at a level which allows for the optimum adsorption of color bodies by the anion exchange resins. The pH of the sugar solution prior to decolorization depends on previous processing steps. It is desirable to contact the anion exchange resin and the sugar solution at a pH ranging from about 1 to about 7, preferably about 3 to about 6, and more preferably about 4 to about 5.

The amount of dissolved sugar present in the sugar solution will vary with the sugar source. The amount of dissolved sugar ranges up to about 70 weight percent with about 20 to about 50 weight percent being more preferred.

After the resin has been loaded with color bodies, the resin can be regenerated using known techniques. For example, the resin can be regenerated by first contacting the resin with an aqueous solution of sodium chloride and either an alkali metal or alkaline earth metal hydroxide (required to convert resin to hydroxide ion form) and then contacting the resin with an aqueous solution of either sodium chloride or hydrochloric acid (required to convert resin to desired hydrochloric acid form for subsequent decolorization of sugar solution).

The following example illustrates but does not limit the scope of this invention.

EXAMPLE

For each of three runs, a 100 ml sample of macroporous, chloromethylated styrene-divinylbenzene (6 weight percent divinylbenzene) copolymer beads is washed with 100 ml of methanol in a Buchner funnel and air dried overnight. For the first run, 16 g (85 meq/CH₂Cl) of the dried beads are swelled in 75 ml of methylal for 1 hour at 44° C. in a 250 ml, 3-necked flask fitted with a stirrer, condenser and dropping funnel. For the second run, 16 g of the dried copolymer beads are swelled in 70 ml of ethylenedichloride (EDC) at 50° C.

For each of the first two runs, a mixture of 34 ml (0.5 moles) ethylenediamine (EDA) and 35 ml of methanol are added dropwise to the slurried beads over 1 hour as the slurry is agitated. After finishing the addition of the EDA, the reaction mixture is stirred for three hours.

For the first run, the reaction temperature is controlled between 44° to 45° C. For the second run, the reaction temperature is controlled between 55° to 60° C.

The reaction mixture is filtered and the aminated resin is washed with excess methanol and then with excess water. The washed resin is stirred in 200 ml of 1.0N NaOH for 1 hour and backwashed to neutral pH. The free base form of the resin for the first two runs has the properties illustrated in Table I.

TABLE I

Properties of Polyamine-Functionalized Anion Exchange Resins	Swelling Solvent	
	Methylal	EDC
Weak Base Capacity, meq/ml	1.62	1.47
Strong Base Capacity, meq/ml	0.1	0.03
Water Retention Capacity, percent	49	52
Dry Weight Capacity, meq/g	5.3	4.69
Porosity, cc/g	0.56	0.68

For the third run, the copolymer beads are swollen in EDC and aminated with diethylenetriamine (DETA) under conditions substantially similar to the conditions described for the first two runs.

The decolorizing capacity of each of the polyamine-functionalized resins is measured by pumping high fructose corn syrup (50 weight percent dissolved solids) or acidified sugar beet syrup (35 weight percent dissolved solids at pH=4.5) through 5 cc of the resin in a 1 cm x 5 cm glass column at 2.4 bed volumes/hr at 50° C. The concentration of color bodies in the syrup exiting the column is continuously monitored by a UV spectrophotometer at 420 nm. This concentration is divided by the concentration of color bodies in the syrup entering the column to determine the percent color leakage.

FIGS. 1-3 plot a comparison of the percent color leakage for each resin and for a conventional weak base anion exchange resin. The conventional resin is prepared by aminating a macroporous, chloromethylated copolymer of styrene and divinylbenzene with dimethylamine, sold commercially by The Dow Chemical Company under the trademark DOWEX 66. Cycle 1 is the percent color leakage for the fresh resin in the HCl form. Cycle 2 is the percent color leakage for the resin after loading the resin to 50 percent color leakage and then regenerating with 1.0N NaOH and 1.0N HCl.

FIGS. 1-3 illustrate a significant reduction in color leakage for each of the polyamine-functionalized resins relative to the color leakage of a conventional anion exchange resin.

What is claimed is:

1. An improved process for decolorizing an aqueous sugar solution by contacting the solution with an anion exchange resin, the improvement comprising using an adsorbent anion exchange resin prepared by aminating a macroporous, chloromethylated copolymer with a polyamine with amine groups selected from primary and secondary amine groups and a combination thereof under conditions sufficient to promote crosslinking of

unreacted amine sites with chloromethyl groups on the copolymer.

2. The process of claim 1 wherein the polyamine is aliphatic.

3. The process of claim 2 wherein the aliphatic polyamine is a diamine.

4. The process of claim 3 wherein the aliphatic diamine is ethylene diamine or 1,3-diaminopropane.

5. The process of claim 1 wherein the macroporous, chloromethylated copolymer is aminated in the presence of a polar solvent.

6. The process of claim 5 wherein the polar solvent is water or methanol.

7. The process of claim 1 wherein macroporous, chloromethylated copolymer is aminated continuously at a rate sufficient to control the temperature of the exothermic amination reaction.

8. The process of claim 1 wherein the macroporous, chloromethylated copolymer is a crosslinked aromatic copolymer.

9. The process of claim 8 wherein the crosslinked aromatic copolymer is a copolymer of a polyunsaturated monomer and a monoethylenically unsaturated monomer.

10. The process of claim 9 wherein the polyunsaturated monomer and the monoethylenically unsaturated monomer comprise at least 50 weight percent of an aromatic monomer.

11. The process of claim 10 wherein the polyunsaturated monomer is divinylbenzene, trivinylbenzene or ethylene glycol diacrylate.

12. The process of claim 10 wherein the monoethylenically unsaturated monomer is styrene, α -methylstyrene, vinylpyridine, vinyltoluene, vinylbenzyl chloride, vinylnaphthalene or methyl methacrylate.

13. The process of claim 10 wherein the copolymer is a copolymer of up to about 99.75 weight percent styrene with the balance divinylbenzene.

14. The process of claim 1 wherein the aqueous sugar solution is a solution of corn syrup, a fruit juice or dextrose.

15. The process of claim 1 wherein the aqueous sugar solution is contacted with the anion exchange resin continuously in a packed column.

16. The process of claim 1 wherein the residence time for contact between the anion exchange and the sugar solution is about 0.17 hours to about 0.5 hours.

17. The process of claim 1 wherein the amount of anion exchange resin is from about 0.017 to about 0.008 kg/kg aqueous sugar solution.

18. The process of claim 1 wherein the pH of the sugar solution is about 4 to about 5.

19. The process of claim 1 wherein the amount of dissolved sugar in the sugar solution is about 20 to about 50 weight percent.

20. The process of claim 1 wherein the aqueous sugar solution comprises a solution of high fructose corn syrup.

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